A Study of Phosphate Adsorption on Kaolinite by ^{31}P NMR Spectroscopy

^{31}P NMR을 이용한 카올리나이트에 흡착된 인산염의 연구

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ABSTRACT : To study phosphate adsorption on kaolinite, ^{31}P MAS NMR (magic angle spinning nuclear magnetic resonance spectroscopy) has been used for kaolinite reacted in 0.1 M phosphate solutions at pH's from 3 to 11. There are at least 3 different forms of phosphate on kaolinite. One is the phosphate physically adsorbed on kaolinite surface (outer-sphere complexes) or species left after vacuum-filtering. The second is the phosphate adsorbed by ligand exchange (inner-sphere complexes), and the third is Al-phosphate precipitates which are pH dependent. Most of the inner-sphere complexes and surface precipitates are mainly on hydroxided Al (aluminol) rather than hydroxided Si (silanol). These are pertinent with the results obtained from the phosphate adsorption experiments on silica gel and γ-Al$_2$O$_3$ as model compounds, respectively. The two peaks with more negative chemical shifts (more shielded) than the ortho-phosphate peak (positive chemical shift) are assigned to be the inner-sphere complexes and surface precipitates. The ^{31}P chemical shifts of the Al-phosphate precipitates are more negative than those of inner-sphere complexes at a given pH due to the larger number of P-O-Al linkages per tetrahedron. The chemical shifts of both the inner-sphere complexes and surface precipitates become progressively less shielded with increasing pH. For the inner-sphere complexes, decreasing phosphate protonation combined with peak averaging by rapid proton exchange among phosphate tetrahedra with different numbers of protons is thought to be the reason for the peak change. The decreasing shielding with increasing pH for surface precipitates is probably due to the decreasing average number of P-O-Al linkages per tetrahedron combined with decreasing protonation like inner-sphere complexes.

Keywords : phosphate adsorption, kaolinite, NMR spectroscopy.

요약 : pH 3부터 11까지의 0.1 M 인산염 용액에 카올리나이트를 반응시킨 후 ^{31}P MAS NMR을 이용하여 카올리나이트에 흡착된 인산염을 연구하였다. 카올리나이트에는 적어도 3개 이상의 다른 인산염 환경이 존재하는 것으로 나타났다. 첫 번째는 카올리나이트 표면에 물리적으로 결합되거나(외부권 복합체, outer-sphere complexes) 진공펌프로 시료를 거를 때 남은 용액에서 침전된 인산염이며 두번째의 인산염은 리간드 교환으로 표면에 흡착된 종(내부권 복합체, inner-sphere complexes)이며 마지막 하나는 pH에 밀접한 연관 있는 알루미늄-인산염 침전물이다. 대부분의 내부권 복합체와 침전물들은 수화된 실리콘(silanol)보다는 수화된 알루미늄(aluminol)표면에 흡착이 되어있는데 이것은 인산염의 γ-Al$_2$O$_3$와 실리카 젤 표면 흡착 실험에 의하여 확인되었다. 정인산염(orthophoaphate) 보다 좀더 음의 값을 갖는 ^{31}P 화학적이동값(chemical shift)의 두 개의 피크는 내부권 복합체 및 표면의 침전 물로 해석하였다. 이 두 피크 중 좀 더 음의 값을 갖는(more shielded) 피크가 카올리나이트의 표면에

침전된 침전물로서 증가된 P-O-Al의 결합으로 인하여 이러한 값을 갖는다. 내부권 복합체와 표면의 침전물은 pH가 증가함에 따라 피크가 점차적으로 양의 값 방향으로 이동하는 것이 확인되었다. 내부권 복합체의 경우 pH가 증가함에 따라 결합된 수소이온의 수가 증가하고 이들간에 빠른 교환반응이 이러한 피크의 변화를 설명하여 주며 표면의 침전물의 경우는 내부권 복합체의 경우처럼 수소이온의 감소와 함께 P-O-Al의 결합이 줄어드는 두 가지의 효과가 복합적으로 작용하는 것으로 보인다.

주요어 : 인산염흡착, 카올리나이트, NMR 분광학.

Introduction

Kaolinite is one of the common minerals in geological and soil environments. Therefore, due to its abundance, the reaction of phosphate with kaolinite can be important in controlling the phosphate solubility by adsorption and precipitation, and, as a result, its fate in the geological environments and its availability to plants in soils (Hingston et al., 1974; van Riemsdijk and Lyklema, 1980a, b). Excessively fertilized soils can be a problem for the phosphate availability and sometimes the excessive inflow of phosphate from soils can cause eutrophism (Pierzynski et al., 1996, Gächter et al, 1998). Phosphate adsorption and precipitation are also very important in many environmental aspects such as disposal of sludges on lands (Hinedi and Chang, 1989; Duffy and van Loon, 1995). Therefore, understanding of adsorption mechanisms on the molecular scale is necessary to understand the large scale behavior of phosphate. Even though many different methods have been tried, the study of molecular adsorption on mineral surface is not easy (Brown et al., 1999). Spectroscopic methods have proved to be successful. However, some of the methods such as X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy are "ex-situ" and require vacuum condition which cannot represent the real adsorption environments. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and chemical analyses have been the most common conventional methods of investigating phosphate-mineral interactions to identify the precipitates and determine the factors controlling precipitation (van Riemsdijk and

Lyklema, 1980a, b; Traina et al., 1986a, b). However, more crystallized solid phases than geological environments are required to study by those methods. Infrared spectroscopy is one of the methods used in the study of phosphate adsorption (Nanzyo, 1986; Tejedor-Tejedor and Anderson, 1990) even though it has the problem that most of the IR signals are from the matrix, hiding the signals from the surface. However, CIR fourier tranform infrared spectroscopy "in situ" spectroscopic study has shown that this method can be applied to studying surface environments (not vacuum) (Tejedor-Tejedor and Anderson, 1990). Tejedor-Tejedor and Anderson (1990) showed that there are protonated and non-protonated bidentate and non-protonated monodentate phosphate complexes on the surface of "in situ" goethite in aqueous suspensions.

Some other spectroscopic methods can be used for the "in situ" examination, including electron spin resonance, NMR, X-ray Absorption spectroscopy. NMR is a very good tool to study the mineral surface reactions because it provides not only the local environments of molecules adsorbed on mineral surfaces but also the dynamic information on those molecules. For NMR study, many isotopes including ^{133}Cs have been successfully applied to investigation of the molecular surface reactions (Kim et al., 1996a, b; Kim and Kirkpatrick, 1997). ^{31}P is a very effective isotope for NMR study because it is 100% natural abundant and has spin I = 1/2 with very strong signals even though the chemical shift range is rather narrow. There have been several mineral surface reaction studies using ^{31}P NMR. Surface phosphate species from the soil, sludge, and sludge-amended soil have

been good candidates for ^{31}P NMR studies (Hinedi and Chang, 1989; Duffy and van Loon, 1995). However, direct interpretation of ^{31}P chemical shifts is not easy and the study of phosphate reaction with model compounds is necessary to understand those reactions in a systematic way. Bleam et al. (1991) and Lookman et al. (1994) demonstrated the capability of solid-state ^{31}P NMR in their studies of the adsorption of phosphate on boehmite and aluminum hydroxide. Based on solid-state ^{31}P NMR, Bleam et al. (1991) concluded that inner-sphere surface complexes form between phosphate and the Al atoms of boehmite surfaces. Lookman et al. (1994) investigated the phosphate adsorption on aluminum hydroxids with ^{31}P and ^{27}Al NMR and identified Al-precipitates on the surface.

Kaolinite is a good model compound due to its abundance in geological environments and simple structure. This paper presents detailed insight into phosphate adsorption on kaolinite studied using ^{31}P NMR. Surface adsorbed species are differentiated from surface precipitates and this study shows that ^{31}P NMR is a powerful tool to study phosphate adsorption.

Materials and Methods

Kaolinite from Washington County, Georgia was obtained from the Source Clay Repository of The Clay Minerals Society. Oxide and hydroxide coatings on the kaolinite were removed before surface area measurement using the method of Zachara et al. (1988). Nitrogen adsorption with an ASAP 2400, Micrometrics instrument was used for the surface area measurement and measured surface area is 13.9 m^2/g for the < 2 μm size fraction. The measured surface area of this kaolinite is similar to that in Zachara et al. (1988) (15.6 m^2/g).

Dry powder of 0.5 g kaolinite was mixed with 80 ml of 0.1 M KH_2PO_4 solution at pH 3, 5, 7, 9, and 11 in a Teflon bottle at 25°C for 24 hours in a rocking water bath. Initial pH's were controlled with HCl and KOH and were checked and adjusted four times during reaction.

After reaction, samples were vacuum filtered and dried in an oven in air at 60°C for 5 minutes to prevent possible reaction during slow drying. To eliminate the effects of the reactions occurring during prolonged drying, the NMR spectra were collected as soon as possible after reaction and always within 1 week.

To compare spectra of kaolinite with those of Al-phosphate precipitates under similar conditions, amorphous Al-phosphate was prepared by mixing 0.6 g $AlCl_3$ with 200 ml of 0.1 M KH_2PO_4 solution in a Teflon bottle at 25°C at pH 3, 5, 7, 9, and 11. After 6 hours pH's were adjusted to their original values and the samples were vacuum filtered and dried in air.

Reacted kaolinite at pH 5 was washed with a few drops of deionized water adjusted to pH 5 during vacuum filtering to check the washing effects on phosphate at each surface sites.

Vacuum filtered samples were analyzed for P using inductively coupled plasma (ICP) (Perkin-Elmer Model P2000).

The ^{31}P NMR spectra were obtained at 202.4 MHz using a home-built spectrometer that consists of an 11.7-T superconducting magnet (Oxford Instruments) and a Nicolet model 1280 computer and pulse programmer. At room temperature, the samples were spun at 8~9 kHz in a silicon nitride rotor using a 5 mm probe manufactured by Doty Scientific (Columbia, South Carolina). The excitation pulse was about 4 μs ($\pi/4$) and a 10 s recycle delay was routinely used. No changes in peak shapes or intensities were observed at longer recycle delays. Many scans were required to obtain enough signal, up to 4000. The ^{31}P chemical shifts are reported relative to external 85 wt% H_3PO_4 solution.

Cross polarization (CP) MAS spectra were also collected, and 1 ms and 10 ms contact time were used.

Results and Discussion

The ^{31}P MAS NMR spectra of kaolinite contain 2 to 5 peaks or shoulders indicative of

at least this number of phosphate environments at different pH's (Fig. 1). The environments of surface phosphates on the kaolinite are very sensitive to the pH, indicated by the spectral change with pH. The chemical shifts (peak maxima) are between +5 to -15 ppm, well within the observed range for phosphate and aluminum phosphate materials (Griffiths et al., 1986; Mudrakovskii et al., 1986; Turner et al., 1986; Hayashi and Hayamizu, 1989). However, unique simulation of the ^{31}P spectra obtained in this study has proven to be difficult because of the overlap of broad components.

The spectra of the pH 3 and pH 5 samples contain 5 peaks or shoulders at about +4, +1, -4, -9, and -15 ppm, but at higher pH the spectra are dominated by a peak at positive chemical shifts and also contain peaks or shoulders at negative chemical shifts (Fig. 1). The position of the largest peak changes from about +2.5
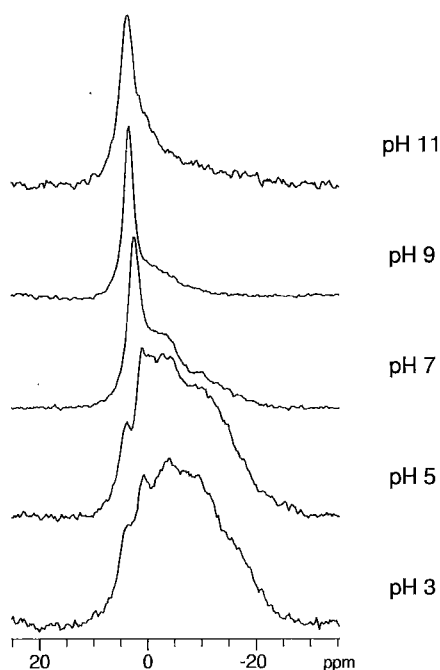

Fig. 1. ^{31}P MAS NMR spectra of kaolinite collected at 11.7 T after adsorption reaction in 0.1 M KH_2PO_4 solution at indicated pH's for 24 hours.

ppm at pH 7 to +4 ppm at pH 11. The relative intensities of the peaks and shoulders with negative chemical shifts and the mean chemical shift of the spectra (the first moment, M1) both become less shielded (more positive) with increasing pH (Fig. 2).

The observed ^{31}P NMR peaks in kaolinite samples must be assigned based on the chemical shifts observed from the model compounds, the known effects of local structure and composition on ^{31}P chemical shifts, and CP and pH effect.

The peaks near +1 and +4 ppm for kaolinite are readily assigned to K-orthophosphates precipitated from residual solution. Solid KH_2PO_4 has a chemical shift of +3.3 to +4.3 ppm and other alkali and alkaline earth orthophosphate salts have positive chemical shifts (Griffiths et al., 1986; Mudrakovskii et al., 1986; Turner et al., 1986; Hayashi and Hayamizu, 1989). The spectra of washed kaolinite with a few drops of water supports this conclusion. Washing with a few drops of water causes the relative intensities in the less shielded (less negative or more positive) peaks to decrease (Fig. 3). For this sample, most of the intensity of the positive peaks is eliminated, and the intensity of the -4 ppm peak is reduced because K-orthophosphates are readily soluble. The kaolinite samples were moist after filtration, and thus, there was less complete removal of the solution from the kaolinite during vacuum filtration. There is no significant change in P concentration with pH and this almost constant wt% P in samples at different pH's may be due to this incomplete filtration (Table 1).

At pH 7, 8, and 11 the peaks with positive chemical shifts are broader and have greater relative intensities than at lower pH's. Most intensity at positive chemical shifts for the pH 7, 9, and 11 samples must be due to K-orthophosphates precipitated from residual solution (the amount of phosphate adsorbed or precipitated should decrease with increasing pH). However, it is also likely that some of the intensity in this range is due to P in inner-sphere com-
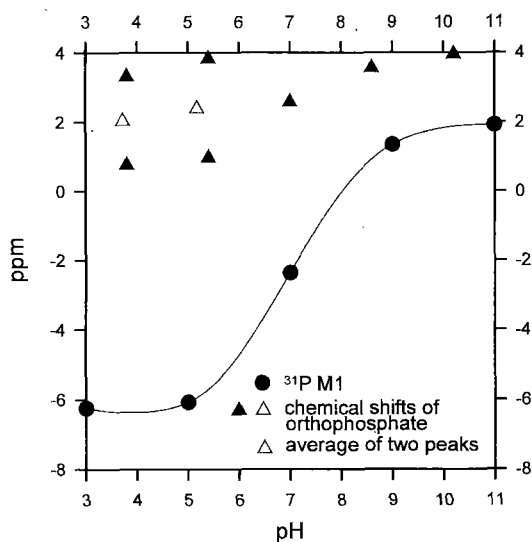
Fig. 2. M1 of ^{31}P NMR spectra of kaolinite as a function pH and concentration (10^{-1} M to 10^{-4} M) of KH_2PO_4 solution, and ^{31}P chemical shifts (peak maximum) of peaks assigned to precipitated orthophosphate as a function of pH in kaolinite exchanged in 0.1 M KH_2PO_4 solution.
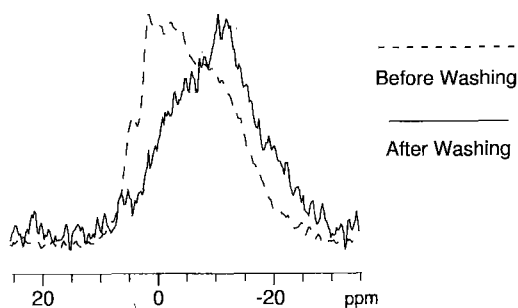

Fig. 3. ^{31}P MAS NMR spectra of kaolinite after washing experiments for the samples after adsorption reaction in pH 5 and 0.1 M KH_2PO_4 solution for 24 hours. Dotted lines and full lines indicate the spectra before and after washing.

plexes (bonded by ligand exchange) which have slightly more negative chemical shifts than the K-orthophosphates.

The weighted average of the positions of the two peaks of positive chemical shifts at pH 3 and 5 and the single peaks at higher pH's show a trend of decreasing shielding with increasing

Table 1. Wt% P in samples after reaction in 0.1 M phosphate solution at the listed pH's.

pH	3	5	7	9	11
wt% P	0.22	0.26	0.24	0.24	0.22

pH (Fig. 2). This trend is consistent with the expected decreasing protonation of orthophosphate with increasing pH. More protonated orthophosphate species dominate at lower pH in solution and the orthophosphates precipitated from solution should vary in a similar way (more protonated orthophosphate precipitation at lower pH). The chemical shifts of the orthophosphates K_3PO_4, K_2HPO_4, and KH_2PO_4 are 11.7, 4.9, and 3.3 ppm, respectively (Grimmer and Haubenreisser, 1983) and that of H_3PO_4 solution at room temperature is 0 ppm. If there is rapid exchange of protons among these species (as proposed for surface adsorbed P species by Bleam et al., 1991) or if the peaks for these environments overlap, the observed peak maximum will be the average chemical shift.

The relative intensity at positive chemical shifts increases with CP-MAS at a contact time of 1 ms (Fig. 4). At a 10 ms contact time, there is no intensity at negative chemical shifts and there is only a single peak with a maximum at 2.3 ppm. The spectra show that these sites with positive chemical shifts are probably less protonated than the sites with negative chemical shifts or that their P-H distances are longer. In addition, the chemical shifts for P with P-O-Al linkages are also usually negative.

All the peaks with negative chemical shifts at lower pH and some of the intensity at positive chemical shifts at higher pH are assigned to phosphate tetrahedra with P-O-Al linkages. Model compounds yielding negative ^{31}P chemical shifts all contain phosphate with either P-O-Al or P-O-P linkages (Cheetham et al., 1986; Turner et al., 1986). Al, alkali Al, and alkaline earth Al phosphates typically have chemical shifts in the range −4 ppm to −30 ppm (Mudrakovskii et al., 1986; Turner et al., 1986; Bleam et al., 1989a, b; Hayashi and Hayamizu, 1989). The
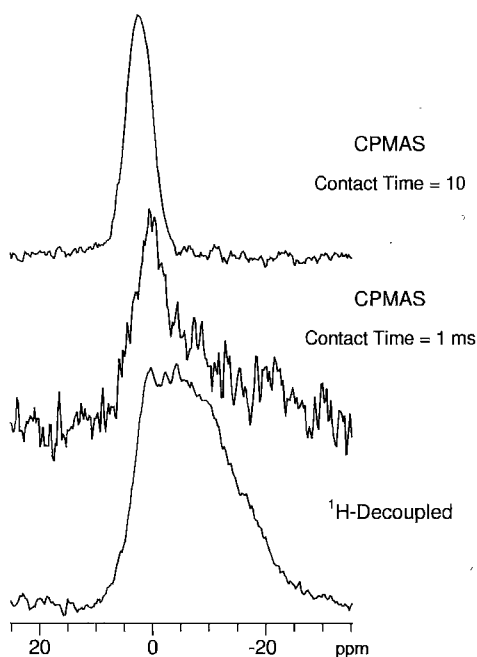
Fig. 4. ^{31}P CP-MAS and proton decoupled NMR spectra of kaolinite collected with different contact times at 11.7 T after adsorption reaction in 0.1 M KH$_2$PO$_4$ solution at pH 3.

Fig. 5. ^{31}P MAS NMR spectra of silica gel and γ-Al$_2$O$_3$ collected at 11.7 T after adsorption reaction in 0.1 M KH$_2$PO$_4$ solution at pH 5 for 24 hours.

peaks and shoulders in the spectra of kaolinite with negative chemical shifts are thus certainly due to P in PO$_4$ tetrahedra with one or the other of these linkages. Polymerized phosphates are rare in natural environments and in experiments with sufficient alkali, alkaline earth, and Al. The intensity at negative chemical shifts at low pH is most likely due to P with P-O-Al linkages, probably with additional P-O-K and P-O-H linkages.

The possibility of Si-O-P linkages in kaolinite is excluded. The oxygens in Si-O-P linkages are overbonded, and there are few compounds with such linkages. An additional adsorption experiment was carried out with a high surface area silica gel (surface area, 390 m^2/g) and γ-Al$_2$O$_3$ (surface area, 104 m^2/g) at pH 5. Spectrum of silica gel has one big orthophosphate peak and very small peak which can be hardly recognized were observed (Fig. 5). However, the adsorption experiment with a high surface area
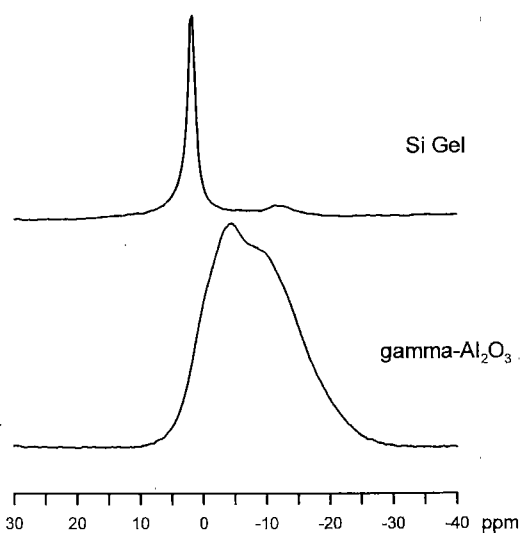
γ-Al$_2$O$_3$ (surface area, 104 m^2/g) at pH 5 show two peaks with negative chemical shifts like those in kaolinite (Fig. 5), indicating that most of phosphates on kaolinite are adsorbed or precipitated on almuminols (hydroxided Al) rather than silanol (hydroxided Si).

The peaks near −9 ppm and the unresolved intensity at more negative chemical shifts present at pH 3 and 5 can be assigned to P environments which have more P-O-Al linkages per tetrahedron than those with chemical shifts near -5 ppm. Al orthophosphate model compounds have more shielded chemical shifts than alkali and alkaline earth orthophosphate (Müller et al., 1984; Turner et al., 1986). In addition, the chemical shifts of most small, highly charged cations in oxides become more negative with increasing average electronegativity of their next-nearest neighbor cations (Turner et al., 1986; Engelhardt and Michel, 1987). Thus an increasing number of P-O-Al linkages per tetrahedron correlates with more negative ^{31}P chemical shifts.

Much of the ^{31}P spectral intensity is due to surface adsorbed phosphate in inner-sphere complexes and most of these complexes are pro-

tonated. The peak near −5 ppm at pH 3 and 5 and part of the intensity at chemical shifts from −3 to +3 at higher pH were assigned to surface adsorbed phosphate complexes with monodentate linkages to the surface. At high solution concentrations like this experimental condition, bidentate complexes are not expected to occur (Rao and Sridharan, 1984; Tejedor-Tejedor and Anderson, 1990). However, the peak near −9 ppm at pH 3 and the unresolved intensity in this range and at more negative chemical shifts, and possibly the intensity in the −10 to −3 ppm range at pH 9 and pH 11 are assigned to surface precipitates with P-O-Al linkages.

Support for this assignment comes from several directions. As described above, the ^{31}P chemical shifts of Al-phosphate surface precipitates are expected to be more negative than those of true surface sites, because they are likely to have more P-O-Al linkages per P tetrahedron than 1 or 2 linkages for monodentate or bidentate surface complexes.

These peaks and unresolved intensity show decreased shielding with increasing pH, and these trends are consistent with both a decreasing number of P-O-Al linkages and decreased protonation in this phase. Single phase, amorphous Al-phosphate precipitates made with KH_2PO_4 and $AlCl_3$ yield one ^{31}P peak with chemical shifts becoming less shielded with increasing pH (−17 ppm at pH 3 to −9 ppm at pH 9, Fig. 6). Those chemical shift ranges are almost similar to those assigned to Al-phosphate precipitates in kaolinite sample. These precipitates probably have compositions and structures different from the precipitates formed in the adsorption experiments because the Al^{+3} contents of the solutions were different. None-the-less, the relatively negative chemical shifts and the direction of the pH variation of the chemical shifts are the same for both.

Additional but weaker support for peak assignments comes from the washing experiments (Fig. 4). Al phosphate precipitates should be less readily soluble than surface adsorbed phosphate, and for kaolinite the relative intensities
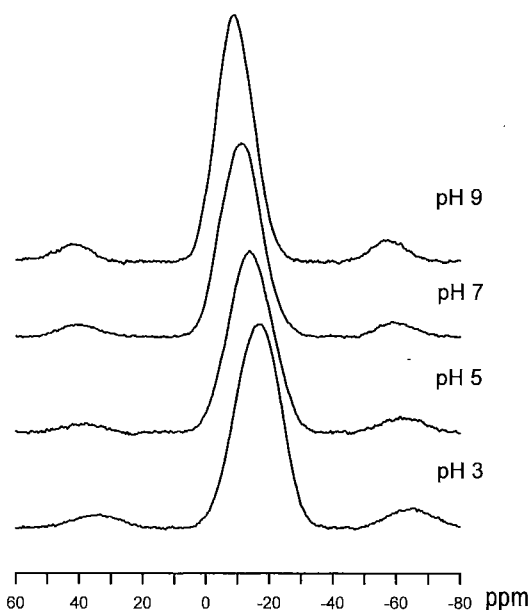

Fig. 6. ^{31}P MAS NMR spectra of synthesized Al-phosphate collected at different pH's at 11.7 T.

at chemical shifts ascribed to surface precipitates increase more than those at surface adsorbed phosphate after washing.

For the peaks assigned to inner-sphere surface complexes, the trends of decreasing shielding with increasing pH are expected due to decreasing protonation of these complexes, as proposed by Bleam et al (1991). IR studies of phosphate adsorbed on goethite in aqueous suspensions support this idea. These IR spectra contain evidence of protonated and non-protonated bidentate and non-protonated monodentate surface phosphate complexes (Harrison and Berkheiser, 1982; Tejedor-Tejedor and Anderson, 1990). And these results also indicate that non-protonated bidentate complexes dominate at high pH and low P-concentration (Harrison and Berkheiser, 1982; Tejedor-Tejedor and Anderson, 1990). Because of the similar chemical behavior of phosphate in Al and Fe^{+3} oxy-hydroxide systems, similar results are expected for kaolinite samples (Hingston et al., 1974). Successive protonation of phosphate groups in Ca and K-orthophosphate model compounds is known to cause more

negative ^{31}P chemical shifts (Rothwell et al., 1980; Grimmer and Haubenreisser, 1983). Thus, at lower pH, surface phosphate complexes are more protonated and have more negative chemical shifts. If there is proton exchange between these different surface complexes at frequencies greater than a few kHz, dynamical averaging will cause the observed chemical shift for surface phosphates with the same number of P-O-Al surface bonds but different number of protons to be the weighted average of the chemical shifts of those different environments. At such high phosphate concentrations used in this experiment, almost all the surface phosphate linkages are expected to be monodentate (Rao and Sridharan, 1984; Tejedor-Tejedor and Anderson, 1990), and changing protonation is the main factor controlling the chemical shift change.

The structure of the Al phosphate precipitates cannot be fully determined due to large peak breadths, but they appear to be amorphous. Different minerals and soils, pH conditions, reaction temperatures, solution concentrations and cations in solution appear to cause formation of many different phosphate precipitates (Kittrick and Jackson, 1956; Tamimi et al., 1963; Kim et al., 1983). Taranakite has been considered to be one of the important precipitation products (Kim et al., 1983), but its structure is not well known. It has ^{31}P chemical shifts of 4.5 ppm, −9.2 ppm, and −18.0 ppm (Bleam et al., 1989b). Kim et al. (1983) made a precipitate by reacting an Al-impregnated cation exchange resin with 0.25 and 1 M KH$_2$PO$_4$ solutions and identified the eventual product as taranakite. They found, however, that the initial reaction product was an amorphous Al-phosphate, and that a more crystalline product developed during incubation or prolonged reaction. Considering the chemical shift range, the spectra of kaolinite samples at pH's 3 and 5 might be consistent with poorly ordered taranakite or an amorphous phase with a similar local structure, but the spectra at higher pH's are clearly not. AlPO$_4$ zeolites containing tetrahedral Al usually have much more negative chemical shifts than those of the

precipitates here (Blackwell and Patton, 1984), but minerals such as wavellite, brazilianite, and crandallite which have octahedral Al have chemical shifts similar to those of the precipitates (−5 to −12 ppm, Bleam et al., 1989a). ^{27}Al MAS NMR spectra of reaction products taken at 11.7 T and MAS frequencies > 10 kHz show only octahedral Al, and thus the Al sites in the precipitates are very likely to have this coordination. Brazilianite and crandallite have P-OH bonds in their structures and contain Na and Ca for charge balance, whereas wavellite contains structural H$_2$O in addition to P-OH bonds.

Based on the results for reacted kaolinite samples and the direct Al-phosphate precipitates, the best interpretation is that the precipitates are amorphous and contain a range of different local phosphate environments with the average number of P-O-Al and P-O-H linkages per tetrahedron decreasing with increasing pH and decreasing solution concentration.

Conclusions

NMR has proven to be a useful tool for investigating surface adsorbed and precipitated phosphate species for kaolinite. It differentiates at least three different phosphate environments, orthophosphate precipitated from the residual solution after vacuum filtering, surface adsorbed phosphate in inner-sphere complexes, and surface Al-phosphate precipitates. For kaolinite, most of the surface reactions with phosphate occur on the aluminol sites rather than silanol sites. Orthophosphate precipitated from residual solution is important at all pH's and surface adsorbed species (inner-sphere complexes) and Al-phosphate precipitates are also important at lower pH ranges. The local structures and compositions of both inner-sphere complexes and surface precipitates are sensitive to pH with the chemical shifts becoming less shielded (less negative) with increasing pH. The observed chemical shifts for the inner-sphere complexes appear to be the weighted averages of primarily

monodentate surface sites with different proto-
nations dynamically averaged by rapid proton
exchange, with greater average protonation at
lower pH's. For the Al-phosphate precipitates,
both decreasing protonation and a decreasing
number of P-O-Al linkages with increasing pH
and decreasing phosphate solution concentration
probably contribute to the chemical shift changes.

Acknowledgments

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