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The Intercalation Reaction of 1,10-Phenanthroline with Layered Compound $FePS_3$

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The intercalation reaction of 1,10-phenanthroline with $FePS_3$ in ethanol and in the presence of anilinium chloride has been monitored in detail with the X-ray powder diffraction (XRD) method to study the reaction mechanism. It is revealed that during the intercalation period there are three phases: the 001 phase (corresponding to the perpendicular orientation of the 1,10-phenanthroline ring with the layer of the host $FePS_3$), the 001′ phase (standing for the parallel orientation of the 1,10-phenanthroline ring with the layer), and the 001″ phase (pristine $FePS_3$), but as the period of the reaction is prolonged, the 001′ and 001″ phases diminish gradually and finally disappear, and the 001 phase is intensified and a complete intercalate is obtained for Series A, in which excess 1,10-phenanthroline is used. However, for Series B in which the optimum amount of 1,10-phenanthroline is used, the 001 and 001″ phases diminish gradually, and another intercalate is obtained that exhibits the 001′ phase. Moreover, if the amount of phenanthroline used in the reaction is more than that in Series B but not in excess, another intercalate containing 001 and 001′ phases is obtained. In these intercalation reactions, the results of IR spectroscopy indicate that anilinium chloride serves only as the source of protons for 1,10-phenanthroline, but 1,10-phenanthroline acts as both the complexing agent of Fe^{2+} ions removed from $FePS_3$, confirmed by UV spectra of the filtrates, and the inserted guest, some of which exists in the form of protonated cation to maintain the charge balance of the intercalates. From the experimental evidence we find that the arranged orientation of 1,10-phenanthroline between the layers is controlled by the amount of guest used in the reaction, and a possible intercalation mechanism is proposed for the reaction.

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Key Words: **intercalation; $FePS_3$; 1,10-phenanthroline; mechanism.**

INTRODUCTION

Intercalation of organic species into layered inorganic solids provides a useful approach to creating ordered organic–inorganic nanocomposite materials with novel properties compared with the parent compounds, and hence has attracted considerable attention in recent years (1). The transition metal phosphorus trisulfides MPS_3, where M stands for a metal in the 2+ oxidation state (M = Mn, Fe, Co, Ni, Zn, Cd, etc.), are layered compounds made up of two-dimensional arrays of $P_2S_6^{4-}$ bridging ligands coordinated to the M^{2+} cations which have monoclinic structure ($C2/m$) based on the $CdCl_2$ type, in which the M^{2+} ions and the center of the P–P pairs occupy the Cd positions and the sulfur ions occupy the chloride positions (2). The MPS_3 phases containing some paramagnetic M^{2+} ions (Mn^{2+}, S = 5/2; Fe^{2+}, S = 2; Ni^{2+}, S = 1) show normal two-dimensional antiferromagnetism with Nèel temperatures of 78, 120, and 253 K, respectively (3–5). The lamellar MPS_3 compounds undergo two types of intercalation reaction. One is redox intercalation involving electron donation from guest to host, similar to that of the metal dichalcogenides (6). The other is that several MPS_3 (M = Mn, Fe, Cd, Zn) undergo a unique nonredox intercalation reaction based on cation exchange between host and guest, in which M^{2+} cations can leave their intralamellar sites and go into the solution, while guest cations in the solution can be taken up into the interlayer van der Waals gaps to maintain the charge balance of the intercalation compound (7). After intercalation the properties of the intercalates sometimes were dramatically changed. For instance, intercalation of 4′-dimethylamino-N-methylstilbazolium (DAMS) into $MnPS_3$ produced a multifunctional material combining nonlinear optical properties with a second harmonic generation efficiency 300 times as strong as that of urea and ferromagnetic property with $T_c = 40$ K (8).

Recently, considerable success in the elucidation of the structural and physical properties of the intercalation com-

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pounds has been achieved using a combination of X-ray diffraction, neutron diffraction, FT-IR, and solid state NMR (9). The kinetics of the intercalation of some species into crystal $MnPS_3$ was studied using time-resolved *in situ* XRD by O'Hare *et al.* (10), and a mechanism for the intercalation of pyridine into $MnPS_3$ was proposed by Joy and Vasudevan (11). However, little is known about the details of the intercalation process of layered $FePS_3$, and, especially, the factor controlling the orientation of the guest in the van der Waals gap. In this work we study the intercalation of 1,10-phenanthroline into layered $FePS_3$ in detail with powder XRD technology to follow the intercalation process, and propose a possible intercalation mechanism for the reaction based on experimental evidence.

EXPERIMENTAL

X-ray powder diffraction (XRD) patterns were recorded on a Dmaxr A X-ray diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). Infrared spectra were obtained on a Nicolet SX Fourier transform spectrometer. UV–vis spectra were recorded on a Shimadzu UV-1206 spectrometer.

Pure $FePS_3$ was synthesized by reaction of stoichiometric amounts of high-purity elements ($> 99.9\%$) in an evacuated quartz tube at 700°C as described in the literature (12). It was identified by means of XRD and indexed as a monoclinic unit cell (space group $C2/m$), in which $a = 5.934$ Å, $b = 10.280$ Å, $c = 6.722$ Å, $\beta = 107.16^\circ$, $d = 6.439$ Å (13).

The intercalation reactions designed as follows:

Series A: 1.08 g (9×0.12 g) 1,10-phenanthroline and 1.35 g (9×0.15 g) anilinium chloride were dissolved in 90 ml ethanol, which was divided into nine equal parts, and then each part was added into an ampoule containing 0.06 g $FePS_3$ (Nos.1–9).

Series B: 0.21 g (3×0.07 g) 1,10-phenanthroline and 0.45 g (3×0.15 g) anilinium chloride were dissolved in 30 ml ethanol, which was divided into three equal parts, and then each part was added into an ampoule containing 0.06 g $FePS_3$ (Nos. 10–12).

Series C: 0.075 g 1,10-phenanthroline, 0.15 g anilinium chloride, and 0.06 g $FePS_3$ was added in an ampoule containing 10 ml ethanol (No. 13); 0.24 g (2×0.12 g) 1,10-phenanthroline was dissolved in 20 ml ethanol, which was divided into two equal parts, and then one part was added into an ampoule containing 0.06 g $FePS_3$, 0.50 ml acetic acid (No.14), and another part was added into an ampoule containing 0.06 g $FePS_3$ only (neither anilinium chloride nor acetic acid existed) (No. 15). With EDTA as a complexing agent 0.06 g $FePS_3$ and 0.15 g anilinium chloride were placed into an ampoule containing 10 ml water as a solvent (No. 16). In No.17, the reagents and the solvent were almost same as in Nos. 1–9 of Series A except 0.15 g 5-nitro-1,10-phenanthroline instead of 1,10-phenanthroline was used.

All the ampoules were sealed under vacuum and the mixture was stirred at a constant temperature of 65°C for different periods (Table 1). All samples were treated with the same procedure, in which the mixture was filtered off, and the solids were washed with 15 ml ethanol and 15 ml water several times, and then dried in air. Black powder solids were obtained.

RESULTS AND DISCUSSION

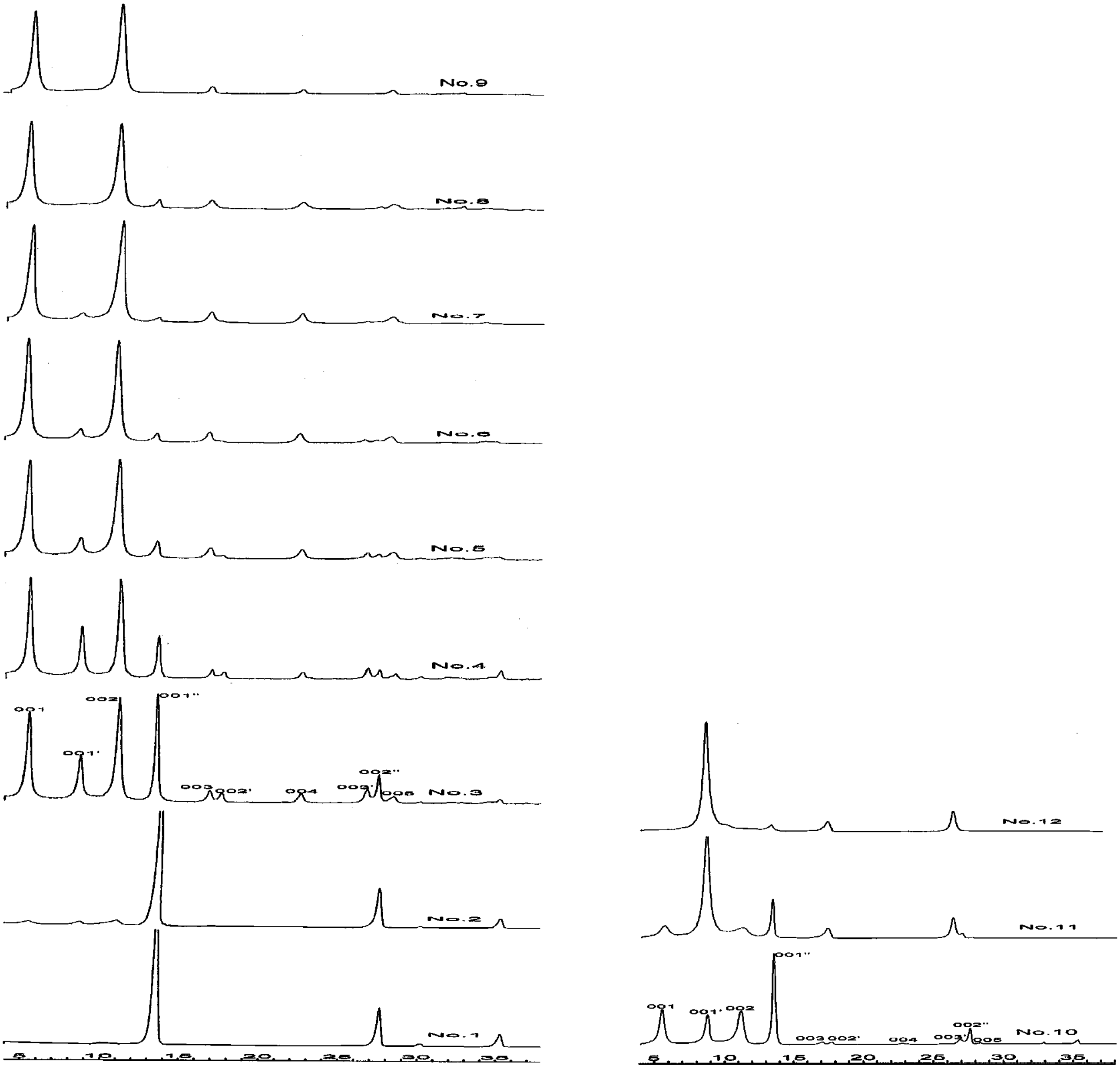
X-Ray Powder Diffraction

Series A. Figure 1 shows the XRD patterns of the nine samples in series A. At the early stage (Nos. 1 and 2), only those patterns corresponding to pure $FePS_3$ (001″ phase) are observed. After 1 day of reaction (No. 3), there are three phases: the 001 phase (the smallest 2θ is about 5.7° corresponding to the biggest lattice space of 15.49 Å), indicating the perpendicular orientation of the 1,10-phenanthroline molecular ring to the layer of the host; the 001′ phase (the smallest 2θ is about 8.9° corresponding to the biggest lattice space of 9.93 Å), indicating the parallel oritnetation of the 1,10-phenanthroline molecular ring to the layer; and the 001″ phase (the smallest 2θ is about 13.7° corresponding to the biggest lattice space of 6.46 Å) is pristine $FePS_3$. As the period of intercalation is prolonged, XRD reflections of the 001′ and 001″ phases gradually diminish and the 001 phase is strengthened. Finally, the reflections of the 001′ and 001″ phases disappear and an intercalate showing only the 001 phase is obtained.

Series B. At the beginning of the intercalation, the XRD results exhibited reflection patterns similar to those of Series

TABLE 1
Reaction Period of the Experiment

	8 h	15 h	1 day	2 days	3 days	4 days	6 days	9 days	15 days	20 days	30 days	40 days	50 days	60 days
Series A	1	2	3	4	5	6	7	8	9					
Series B			10							11		12		
Series C											16	14	13	15
												17		



Series A *Series B*

FIG. 1. Powder XRD patterns used to monitor the intercalation of $FePS_3$ with 1,10-phenanthroline.

A (001 phase, 001′ phase, and 001″ phase), but the relative intensities of the reflections are different from those in Series A, and the diminishing rate of the reflections of the 001″ phase is obviously slower than that of Series A (Fig. 1). As the intercalation continues, the reflections of the 001 and 001″ phases are weakened and the 001′ phase is strengthened. Finally, another intercalate is obtained that exhibited only the 001′ phase.

Series C. For No. 13 a series of 001 and 001′ phase reflections are observed, which indicates that this is an intercalate containing the 001 and 001′ phases (Fig. 2). When acetic acid is used instead of anilinium chloride (No. 14), the XRD reflection exhibits results similar to those of No. 9. But for Nos. 15 and 16 the XRD reflections exhibit the same results as pure $FePS_3$, indicating no intercalation occurs.

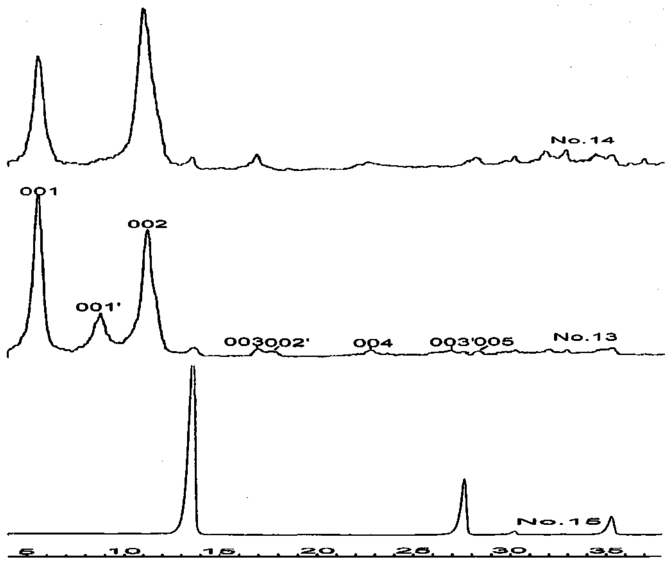


FIG. 2. Power XRD patterns of some samples in Series C.

IR and UV- Vis Spectra

Figure 3 gives the IR spectra of some samples (partial and complete intercalates) of Series A and Series B. Absorption at 570 $\mathrm{cm^{-1}}$ is attributed to the $\nu(\mathrm{PS_3})$ asymmetric stretching band of pristine $\mathrm{FePS_3}$ (001″ phase) (14). While the intercalation is going on its relative intensity decreases. The absorption of the (partial or complete) intercalates occurring at around 606, 582, and 556 $\mathrm{cm^{-1}}$ originates from the splitting of 570 $\mathrm{cm^{-1}}$ of pure $\mathrm{FePS_3}$, which reflects the presence of intralamellar $\mathrm{Fe^{2+}}$ ion vacancies (15, 16).

IR spectra also provide evidence for the presence of guest species. The spectra of Series A and Series B show strong characteristic ring frequencies of protonated phenanthroline or phenanthroline around 1616, 1593, 1421, 841, and 721 $\mathrm{cm^{-1}}$ (17–19). In addition, the absorption bands of the samples show some indiscernible adsorption frequencies of neutral phenanthroline and protonated phenanthroline, but these adsorption frequencies are obviously different from those of anilinium chloride, which are listed in Table 2 including some characteristic IR adsorption frequencies of Intercalate No. 9, phen·$\mathrm{HClO_4}$, neutral phenanthroline (17–19), and anilinium chloride (20, 21) for comparison. So the IR results indicate that the guest inserted into the host $\mathrm{FePS_3}$ is phenanthroline, some of which exists in the form of protonated phenanthroline between the layers of $\mathrm{FePS_3}$ to balance the charge neutrality of the intercalates.

The filtrates of all the samples are the same red color except Nos. 16 and 17. In the light of the UV–vis spectra, the largest absorption wavelength is about 510 nm which is the characteristic absorption of $\mathrm{Fe(phen)_3^{2+}}$ (22), indicating the occurrence of $\mathrm{Fe(phen)_3^{2+}}$ in the filtrate. So in this intercalation 1,10-phenanthroline also acts as a complexing agent for $\mathrm{Fe^{2+}}$ removed from the intralayer of the host $\mathrm{FePS_3}$.

Possible Intercalation Mechanism

From the experimental results we propose a possible intercalation mechanism for 1,10-phenanthroline inserted

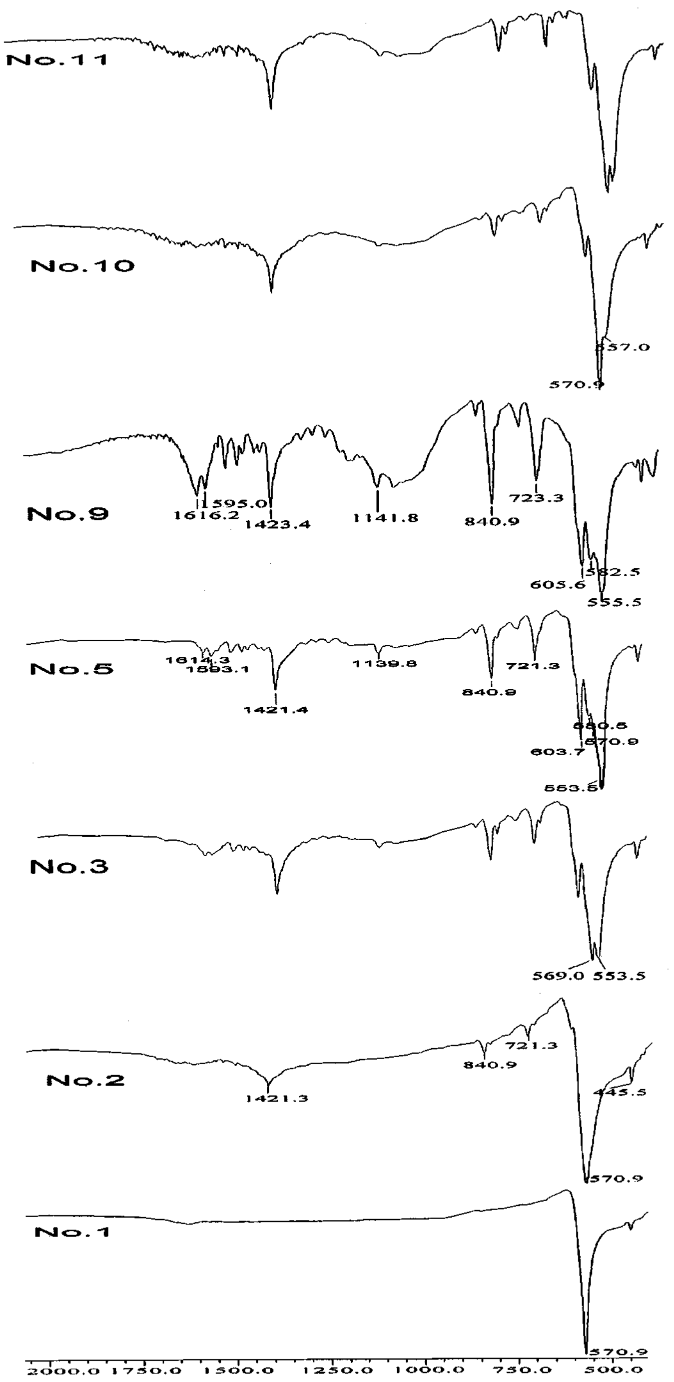


FIG. 3. IR spectra of some samples in Series A and Series B.

TABLE 2

Comparison of the IR Absorption (cm^{-1}) of Intercalate No. 9 with That of Phen·H_2O (17), Phen·$HClO_4$ (18, 19), and $PhNH_2$·HCl

Assignment	Phen·H_2O	Phen·$HClO_4$	No. 9	$PhNH_2$·HCl
Ring str.	1615m	1618w	1616m	
	1585w	1599w	1595m	1599s
				1560s
			1544s	1539m
	1502s	1502m	1507m	1516m
	1492m	1473s	1494m	1493vs
				1461w
	1422s	1419s	1423vs	
		1370w	1371w	
	1345w	1340w	1340w	1330w
H in planar deformation		1244w	1235w	1299w
	1217w	1228w	1213w	
	1186w	1192w	1185w	1198m
	1137m	1145m	1142m	1123m
	1092s	1088s	1099m	1090m
	1079m		1074m	1080m
				1052w
H out of planar bend	853vs	847s	841vs	
	840s			
	779m	782m	766w	
	738vs			744vs
	724m	717s	723s	
				683s

into $FePS_3$ (see Eqs. [1] to [5]) in Fig. 4). As a mechanism, it should explain all the experimental phenomena observed.

From the IR spectrum (Fig. 3), we find that the $\nu(PS_3)$ asymmetric stretching band at 570 cm^{-1} in pure $FePS_3$ is split into two or three strong sharp absorption frequencies in the range 550–610 cm^{-1}, which reflects the occurrence of intralamellar Fe^{2+} ion vacancies (15). How do the intralamellar Fe^{2+} ion vacancies occur? It is known that in this intercalation the filtrates of the samples exhibit almost the same characteristic red color. The UV–vis absorption spectrum of the filtrate in these intercalations shows a strong broad band around 510 nm, which is the characteristic absorption of $Fe(Phen)_3^{2+}$ (22), indicating the presence of $Fe(phen)_3^{2+}$ in the filtrate. It is clear that 1,10-phenanthroline acting as a complexing agent to remove intralamellar iron ion into the solution during intercalation leads to the occurrence of intralamellar Fe^{2+} ion vacancies (Eq. [2] in Fig. 4).

Now that there exist intralamellar Fe^{2+} ion vacancies, how is the charge neutrality of the intercalates maintained? From the IR spectra it is also found that all the intercalation products (partial or full intercalates) exhibit almost similar characteristic absorption frequencies almost similar to those of 1,10-phenanthroline other than anilinium chloride; this suggests that in this intercalation the guest inserted into the host $FePS_3$ is phenanthroline other than anilinium, where some of the phenanthroline exists in the form of protonated phenanthroline among the layers of $FePS_3$. Therefore, the cation vacancies created by removing Fe^{2+} ion from the intralayer of the host are compensated by the protonated phenanthroline inserted into the interlayer. However, where does the proton come from? In this intercalation, we find that no intercalation occurs without anilinium chloride or acetic acid (No. 15), but if anilinium chloride is used the intercalation occurs. It is obvious that anilinium chloride provides the proton to 1,10-phenanthroline (Eq. [1] in Fig. 4). This is confirmed by another experiment, No. 14, in which a result similar to that of No. 9 is obtained when acetic acid is used instead of anilinium chloride because acetic acid can also provide the proton to 1,10-phenanthroline. Therefore, protonation of 1,10-phenanthroline is necessary for this intercalation, so the driving force for the intercalation is possibly the static charge attraction between the protonated phenanthroline cation and the intralayer anion of the host formed by the departure of the intralayer iron cation (Eq. [3] in Fig. 4).

From the XRD results it is found that three phases coexist for a long time. However, in comparing Series A with Series B, in the beginning their XRD results exhibit only small differences, but as the reaction period increases, the differences become greater. For Series A, from the initial to final intercalation the much stronger reflection intensity of the 001 phase than the 001′ phase, as well as the rapidly diminishing rate of reflections of the 001′ and 001″ phases, indicates that the insertion rate of the 001 phase is very fast due to the excessive amounts of 1,10-phenanthroline. For Series B, the amount of 1,10-phenanthroline used is less than that of Series A, so the relative intensity of the 001 phase is weakened and 001′ phase is strengthened more slowly as the intercalation continues. In addition, from the XRD results we find that the diminishing rate of the 001″ phase (pristine $FePS_3$) in Series A is much more rapid than that of Series B, which suggests that the intercalation rate of Series B is obviously slower than that of Series A. However, no matter how much 1,10-phenanthroline is used, at the beginning of the intercalation the 001 and 001′ phases always coexist, so it can tentatively be concluded that the initial intercalation is the parallel insertion of 1,10-phenanthroline into the layer of $FePS_3$ which is a slow reaction (Eq. [3] in Fig. 4). Once the van der Waals forces holding the layers of the host together are destroyed, 1,10-phenanthroline is much more easily inserted into the layers in a fast reaction, in which the guest is arranged perpendicular to the layer due to the restriction of limited interlayer space of the host (Eq. [4] in Fig. 4). Therefore, the XRD reflections of 001 and 001′ phases exist almost concurrently, but the intensity of the 001 phase is much stronger than that of the 001′ phase in Series A.

In Series A, a final intercalate (No. 9) is obtained that exhibits a new series of sharp 001 reflections (up to 005). As

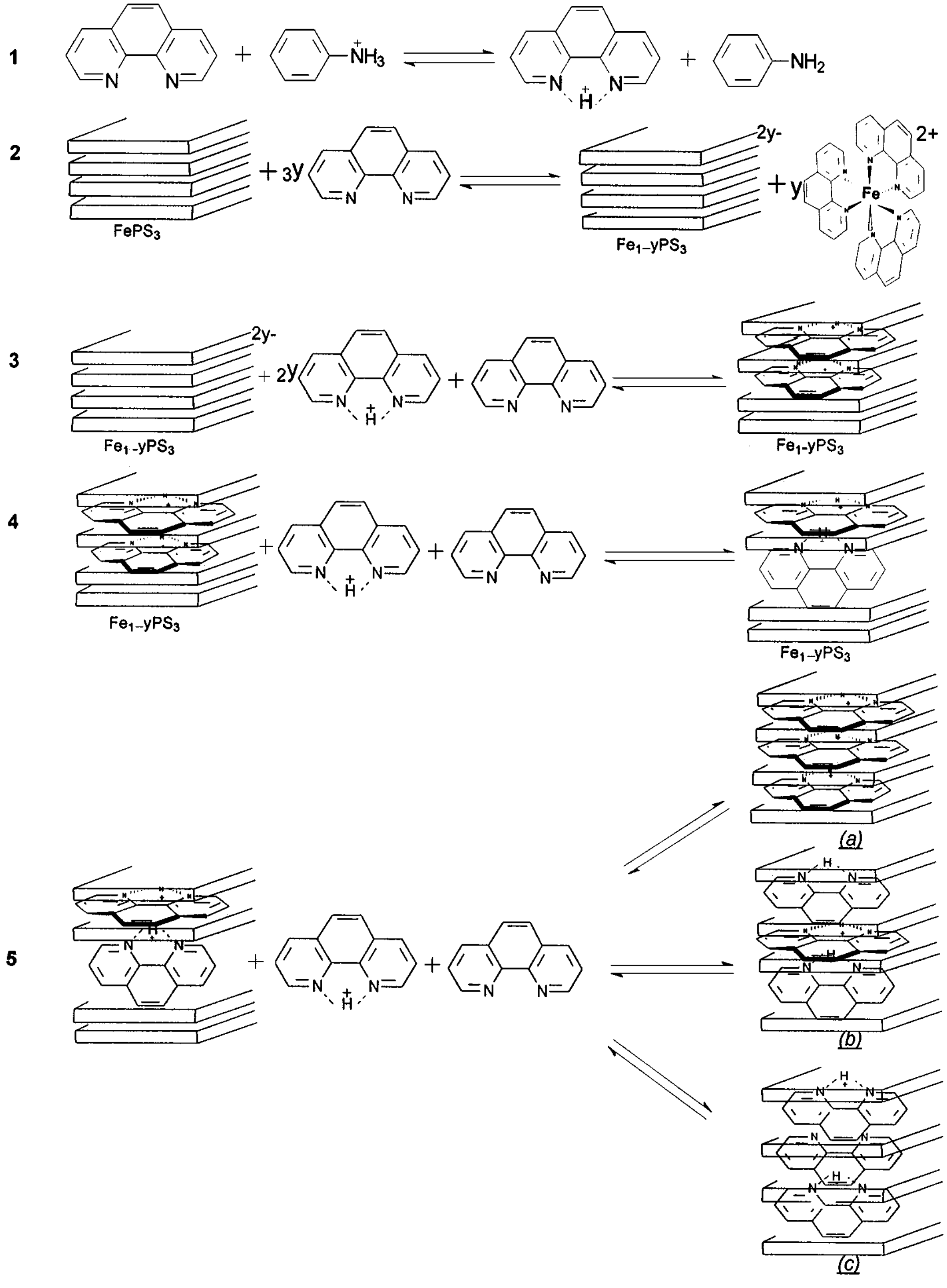


FIG. 4. Intercalation mechanism of 1,10-phenanthroline with layered FePS$_3$. Equation [1]: proton transfer between 1,10-phenanthroline and anilinium chloride. Equation [2]: facial intralayer Fe^{2+} of the host removed initially by 1,10-phenanthroline. Equation [3]: the slower intercalation, in which the protonated 1,10-phenanthroline inserted into the layer to balance charge neutrality is arranged parallel to the layer of the host. Equation [4]: the faster intercalation, where the three phases coexist during the intercalation. Equation [5]: the orientation of the guest controlled by the amount of phenanthroline in the reaction, in which there was a reversible process: (a) molecular ring of phenanthroline is parallel to the layer of the host; (b) the parallel and perpendicular molecular rings of phenanthroline coexist; (c) the 1,10-phenanthroline ring was oriented so that the molecular twofold axis is perpendicular to the layer of the host.

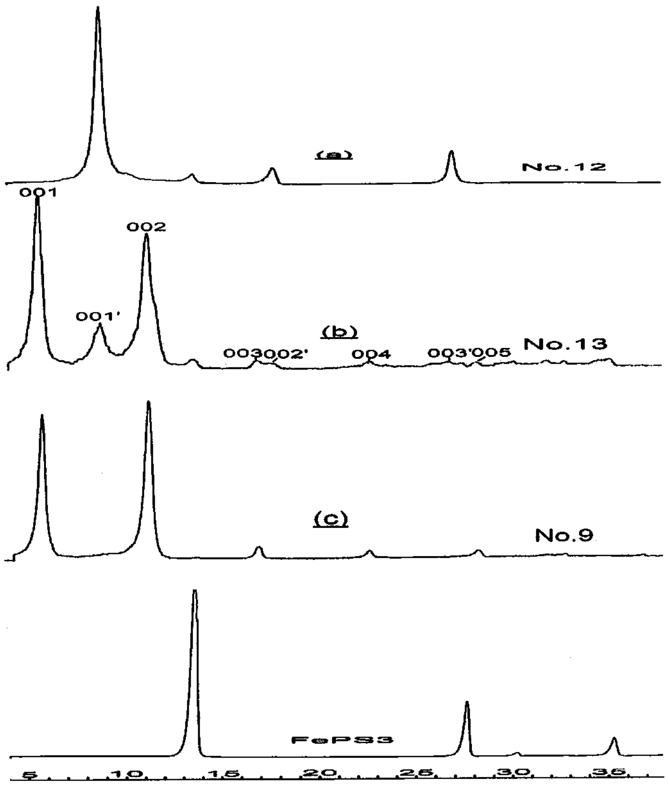


FIG. 5. Comparison of the XRD results of the intercalates in which different amounts of guest were used in the reaction.

a result of intercalation, the lattice spacing increases to 15.49 Å, corresponding to a lattice expansion (Δ*d*) of 9.0 Å with respect to pure $FePS_3$. This suggests that 1,10-phenanthroline ring is oriented in such a direction that the molecular twofold axis is perpendicular to the layer of the host. For Series B, another intercalate (No. 12) is obtained that shows another new series of sharp 001′ reflections (up to 003) exhibiting a lattice spacing increasing to 9.93 Å, corresponding to a lattice expansion (Δ*d*) of 3.5 Å, which indicates orientation of the 1,10-phenanthroline ring parallel to the layers of the host similar to pyridine inserted into $FePS_3$ (23). Moreover, when the amount of 1,10-phenanthroline used in the intercalation is less than that of Series B but not in excess, another intercalate is obtained that contains two phases, 001 and 001′ (No. 13). This indicates that in the intercalation there is a reversible balance process for the guest to be parallel to the layer of the host or perpendicular to the layer, which is controlled by the amount of the guest (Eq. [5] in Fig. 4 and also in Fig. 5).

To explain this possible intercalation mechanism we performed some other experiments. In experiment 15, in the absence of anilinium chloride or acetic acid the XRD reflections are the same as those of pure $FePS_3$, but the color of the solution (in ethanol or acetonitrile) still becomes red, which indicates that the facial Fe^{2+} ions are removed initially by 1,10-phenanthroline confirmed by UV spectroscopy (Eq. [2] in Fig. 4), but no further intercalation occurs owing to the absence of the protonated 1,10-phenanthroline. In experiment 16, in the presence of EDTA as a complexing agent of Fe^{2+} ion, pure $FePS_3$ reacts with anilinium chloride for 1 month and no intercalation is observed which indirectly indicates that it is difficult for anilinium to be inserted into $FePS_3$, and anilinium chloride is only the source of protons for 1,10-phenanthroline. In experiment 17, instead of 1,10-phenanthroline, 5-nitro-1,10-phenanthroline reacts with $FePS_3$ for 2 months under the same conditions as in Series A; XRD shows the same reflections as those of pristine $FePS_3$ and no intercalation occurs, perhaps because the basicity of 5-nitro-1,10-phenanthroline is too weak for anilinium chloride to transfer the proton to it. This also supports the conclusion that the protonation of phenanthroline is one of the keys in affecting intercalation.

CONCLUSION

A new intercalation reaction of 1,10-phenanthroline with layered $FePS_3$ in ethanol and in the presence of anilinium chloride has been studied in detail using powder XRD technology to monitor the intercalation process. In the light of the XRD results a possible intercalation mechanism is proposed which is also supported by the results of IR and UV–vis spectroscopy. When different amounts of 1,10-phenanthroline are used in the intercalation, three different intercalates are obtained, among which the guest inserted into $FePS_3$ is 1,10-phenanthroline other than anilinium chloride; some of phenanthroline exists in the form of protonated cation to maintain the charge balance of the intercalates confirmed by IR spectroscopy. X-ray powder diffraction results also reveal that they are the well-crystallized products. As a result of intercalation, the lattice spacing of one intercalate (001 phase) is expanded by 9. 0 Å with respect to pure $FePS_3$, which indicates that the 1,10-phenanthroline molecular ring is oriented perpendicualr to the layer of the host when excess 1,10-phenanthroline is used in the reaction. The other intercalate (001′ phase) is expanded by 3.5 Å, showing that the guest is parallel to the layer when a suitable amount of phenanthroline is used. However, if the amount of phenanthroline used in the reaction is more than that in Series B but not in excess, another intercalate containing 001 phase and 001′ phases is obtained. It is obvious that the key factor in controlling the orientation of the guest is the amount of 1,10-phenanthroline used in this intercalation.

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