Al$_{1-x}$Fe$_x$PO$_4$ Catalyst: Calcination Behavior

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The calcination behavior of coprecipitated iron–aluminum mixed phosphates having the composition Al$_{1-x}$Fe$_x$PO$_4$, where $x = 0.0, 0.25, 0.5, 0.75$, and 1.0, is investigated by powder X-ray diffraction and ^{57}Fe Mössbauer spectroscopy. It is observed that solid solution formation between FePO$_4$ and AlPO$_4$, which are not isostructural, takes place by incorporation of Fe^{3+} ions into the AlPO$_4$ structure for both Al$_{0.75}$Fe$_{0.25}$PO$_4$ and Al$_{0.5}$Fe$_{0.5}$PO$_4$. Due to this solid solution formation, the phase transformation of AlPO$_4$ from tridymite to the orthorhombic phase takes place at lower temperatures. It is also observed that on solid solution formation the decomposition of FePO$_4$ to Fe$_3$PO$_7$ and α-Fe$_2$O$_3$ is suppressed. The values of the isomeric shift and quadrupole splitting observed for Fe^{3+} ions in the tridymite phase are different from those of the trigonal phase of FePO$_4$. Mössbauer spectra of Al$_{0.75}$Fe$_{0.25}$PO$_4$ in the orthorhombic form show an unresolved quadrupole doublet with $\delta = 0.26$ and $\Delta Eq = 0.25$ mm/sec. In the Al$_{0.25}$Fe$_{0.75}$PO$_4$ sample, incorporation of AlPO$_4$ into the FePO$_4$ lattice takes place on calcination at ≈ 1075 K. The Mössbauer parameters for these samples did not show any change compared to those of the trigonal FePO$_4$. © 1994 Academic Press, Inc.

INTRODUCTION

Aluminum orthophosphate, AlPO$_4$, is a bifunctional catalyst whose surface acid–base sites catalyze various reactions such as dehydration, skeletal isomerization, and alkylation (1). On calcination at 1175 K it crystallizes to the tridymite form (pseudo-hexagonal structure), which on further calcination at higher temperatures transforms into the orthorhombic form at ≈ 1375 K (2). The catalytic properties of AlPO$_4$ vary significantly depending on the method of preparation and the activation temperature. It has been observed that the isomorphous substitution of aluminum or phosphorus in AlPO$_4$ by different poly-charged cations or the combination of AlPO$_4$ with other catalysts can modify its acid–base properties (3–5). Iron orthophosphate, FePO$_4$, which has a trigonal structure (hexagonal type), has also been used as a redox catalyst for a number of reactions, such as oxidative dehydrogenation of isobutyric acid to methacrylic acid, because of the

variable valence states of iron (6). However, the FePO$_4$ catalyst cannot be used for high-temperature reactions as it decomposes to give Fe$_3$PO$_7$, which on further decomposition gives rise to α-Fe$_2$O$_3$. Therefore it is of interest to investigate the stabilization of FePO$_4$ by its incorporation in the AlPO$_4$ lattice of the mixed phosphate of iron and aluminum. The mixed phosphate, if formed, will have both redox and strong acid–base sites which may be useful for a number of chemical reactions. With this view, we have prepared the coprecipitates of Al$_{1-x}$Fe$_x$PO$_4$ (where $x = 0.0, 0.25, 0.5, 0.75$, and 1.0) and studied their temperature-induced crystallization by powder X-ray diffraction (XRD) and ^{57}Fe Mössbauer spectroscopy to determine the composition limits for solid solution formation and the crystal structures of solid solutions.

EXPERIMENTAL

FePO$_4$ and AlPO$_4$ were prepared from aqueous solutions of their corresponding chlorides and H$_3$PO$_4$ (85 wt.%) by precipitation at room temperature with aqueous ammonia. The precipitate was filtered, washed thoroughly with water, and dried in an oven at 400 K for 20 hr. Mixed phosphates, Al$_{1-x}$Fe$_x$PO$_4$, were prepared in the same way by taking the required ratios of aluminum and iron. Calcination behavior of these samples was investigated by heating them at variable temperatures for a fixed duration of 20 hr and then slowly cooling them to room temperature. XRD patterns were recorded using nickel-filtered CuKα radiation. ^{57}Fe Mössbauer spectra were recorded at room temperature using a ^{57}Co/Rh source, and isomeric shift values (δ) are reported with respect to α-Fe at room temperature.

RESULTS AND DISCUSSION

XRD patterns of AlPO$_4$ precipitate, calcined at various temperatures, show that it remains in its amorphous form up to a calcination temperature of 1075 K and gives a broad hump in the range $20° < 2\theta < 40°$. A tridymite form having the pseudohexagonal structure (ASTM 20-44) of AlPO$_4$ is obtained on calcination at 1175 K. Phase trans-

FIG. 1. XRD patterns of $FePO_4$ calcined for 20 hr at (a) 675, (b) 775, (c) 875, (d) 975, and (e) 1175 K.

2 shows the representative ^{57}Fe Mössbauer spectra of iron phosphate recorded at room temperature after calcination at different temperatures. The oven-dried sample shows a quadrupole doublet with isomeric shift $\delta = 0.37$ mm/sec and quadrupole splitting $\Delta Eq = 0.87$ mm/sec. The observed linewidth ($\Gamma = 0.55$ mm/sec) is excessive and is due to the amorphous nature of this sample, as seen from the XRD results reported above. The spectrum remains almost identical up to a calcination temperature of 675 K, as can be seen from Fig. 2b. This value of the isomeric shift is typical of Fe^{3+} in the octahedral environment of oxygen anions. Calcination at higher temperatures leads to decreased values of both the isomeric shift and the quadrupole splitting, as can be seen from Fig. 2c, where the representative spectrum of the sample calcined at 775 K is shown. The sample calcined at 875 K, for which the XRD pattern indicates a trigonal structure, shows $\delta = 0.27$ mm/sec and $\Delta Eq = 0.67$ mm/sec (Fig. 2d), which are in good agreement with the values reported earlier for crystalline $FePO_4$ (7). This value for the isomeric shift is characteristic of Fe^{3+} in the tetrahedral coordination of O^{2-}. The observed linewidth for this sample was found to be ≈ 0.39 mm/sec, which is much less than that obtained for the amorphous form. The change in coordination number is due to removal of water from the lattice (8). The spectrum in Fig. 2e indicates partial decomposition of $FePO_4$ into Fe_3PO_7 on calcination at 975 K. The Mössbauer spectrum of Fe_3PO_7 is fitted as a quadrupole doublet, and the obtained parameters are $\delta = 0.31$ mm/sec and $\Delta Eq = 1.14$ mm/sec, which are in agreement with the values given in the literature (9). The Mössbauer spectrum of the sample calcined at 1175 K is shown in Fig. 2f, which also confirms the formation of α-Fe_2O_3 due to the decomposition of Fe_3PO_7, as seen from

formation of this material to the orthorhombic structure (ASTM 11-550) is initiated on calcination at around 1375 K, and the transformation is complete at ≈ 1475 K. No decomposition of $AlPO_4$ into Al_2O_3 and P_2O_5 is observed up to a calcination temperature of 1475 K. The differential thermal analysis curve of $AlPO_4$ shows loss of water at lower temperatures and a broad endothermic peak beginning at 1307 K and having its maximum at ≈ 1335 K, corresponding to the phase transformation.

It is observed in Fig. 1 that precipitated $FePO_4$ remains in amorphous form up to a calcination temperature of 675 K. The sample calcined at 775 K shows crystallization to an unreported form of $FePO_4$ whose crystal structure could not be ascertained due to its having very few peaks of poor intensity. This material transformed to a trigonal structure (ASTM 29-715) at about 875 K. On further calcination at 975 K for 20 hr, $FePO_4$ partially decomposes to Fe_3PO_7, which further decomposes to α-Fe_2O_3 at around 1175 K by complete evaporation of P_2O_5. Figure
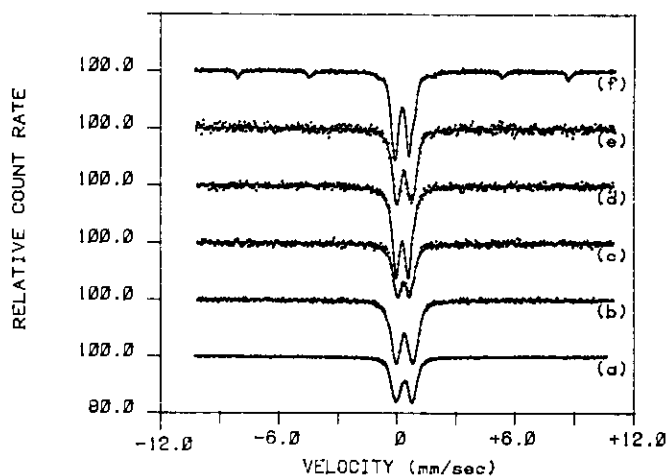

FIG. 2. ^{57}Fe Mössbauer spectra of $FePO_4$ calcined for 20 hr at (a) 400 (oven dried), (b) 675, (c) 775, (d) 875, (e) 975, and (f) 1075 K.
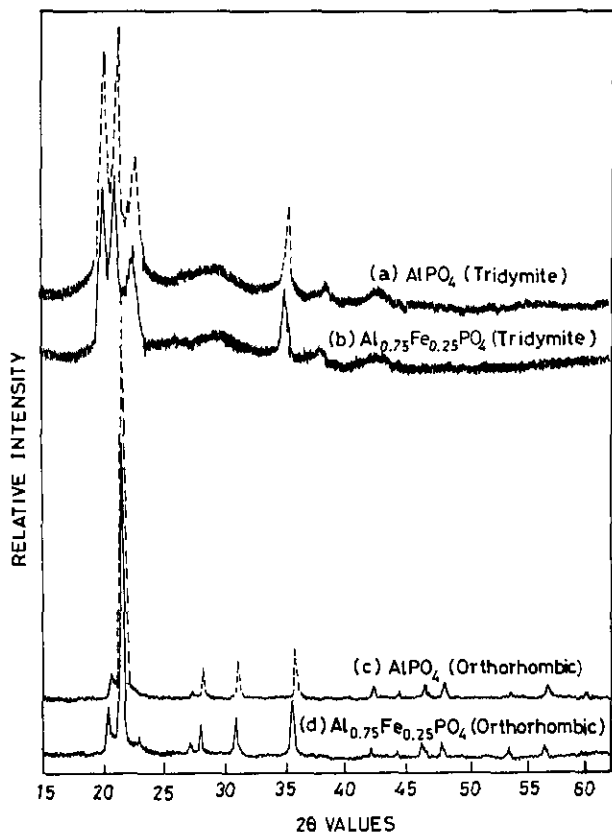
FIG. 3. XRD pattern of the (a) tridymite form of AlPO$_4$, (b) tridymite form of Al$_{0.75}$Fe$_{0.25}$PO$_4$ (calcination at 975 K), (c) orthorhombic form of AlPO$_4$, and (d) orthorhombic form of Al$_{0.75}$Fe$_{0.25}$PO$_4$ (calcination at 1075 K).

the appearance of a magnetic sextet along with a quadrupole doublet of undecomposed Fe$_3$PO$_7$. The values of δ, ΔEq, and the internal hyperfine field obtained from the analysis of the spectrum are 0.40 mm/sec, 0.34 mm/sec, and 518 KOe, respectively, which are characteristic of α-Fe$_2$O$_3$ (10).

Al$_{0.75}$Fe$_{0.25}$PO$_4$ samples calcined at various temperatures show that up to a calcination temperature of 925 K the sample remains in the amorphous state, as shown by XRD patterns. The sample calcined at 975 K shows only diffraction lines for the tridymite phase of AlPO$_4$, and there is no indication of FePO$_4$ as a separate phase. This tridymite form is a solid solution of FePO$_4$ and AlPO$_4$, as there is a detectable increase in the d values of this material as compared to that of AlPO$_4$ in the tridymite form (Fig. 3b). This increase in lattice spacings arises because of the higher ionic radius of Fe^{3+} ($r_{Fe^{3+}} = 0.64$ Å and $r_{Al^{3+}} = 0.54$ Å). The phase transformation of the tridymite form to the orthorhombic form in this mixed phosphate takes place at a much lower temperature ($T =$

1025 K) and is complete by 1175 K. This shows that due to solid solution formation with FePO$_4$ the temperature of the phase transformation of AlPO$_4$ is affected. Further, due to incorporation of FePO$_4$ in the AlPO$_4$ structure, decomposition of FePO$_4$ has not taken place even up to a calcination temperature of 1175 K. The observed lattice parameters of this orthorhombic phase in the mixed phosphate are $a = 7.117$, $b = 7.146$, and $c = 7.058$ Å, while those of orthorhombic AlPO$_4$ are $a = 7.082$, $b = 7.098$, and $c = 6.993$ Å. Figure 3d clearly shows shifts in peak positions of some representative diffraction lines. The Mössbauer spectra of Al$_{0.75}$Fe$_{0.25}$PO$_4$ samples calcined at various temperatures (Fig. 4) show that there is no change in the spectrum up to a calcination temperature of 925 K and that the resolved quadrupole doublet has $\delta = 0.36$ mm/sec and $\Delta Eq = 0.85$ mm/sec. This doublet is characteristic of amorphous FePO$_4$. But there is a significant change in the spectrum of the sample calcined at 975 K (Fig. 4c). It shows two overlapping quadrupole doublets having isomer shift values of $\delta_1 = 0.42$ and $\delta_2 = 0.34$ mm/sec; the corresponding values of the quadrupole splitting are $\Delta Eq = 0.83$ and 0.36 mm/sec. Whereas the larger values of the isomeric shift and quadrupole splitting are consistent with the values observed for amorphous FePO$_4$, the other doublet is due to Fe^{3+} ions present in the tridymite structure. On calcination at higher temperature (1075 K) this spectrum is completely changed and a single unresolved quadrupole doublet having $\delta = 0.26$ mm/sec and $\Delta Eq = 0.25$ mm/sec is obtained (Fig. 4d). This doublet is due to the orthorhombic phase of the mixed-phosphate system. These observations are quite consistent with the XRD results reported earlier. This shows that there are significant changes in the Mössbauer parameters of FePO$_4$ incorporated in the tridymite form of AlPO$_4$. Further, the transformation to the orthorhombic structure leads to a
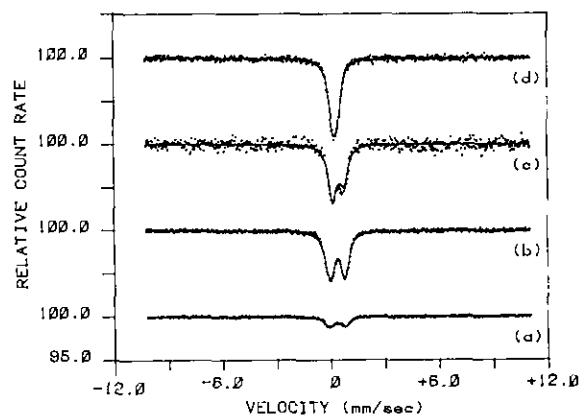

FIG. 4. ^{57}Fe Mössbauer spectra of Al$_{0.75}$Fe$_{0.25}$PO$_4$ calcined for 20 hr at (a) 400 (oven dried), (b) 775, (c) 975, and (d) 1075 K.
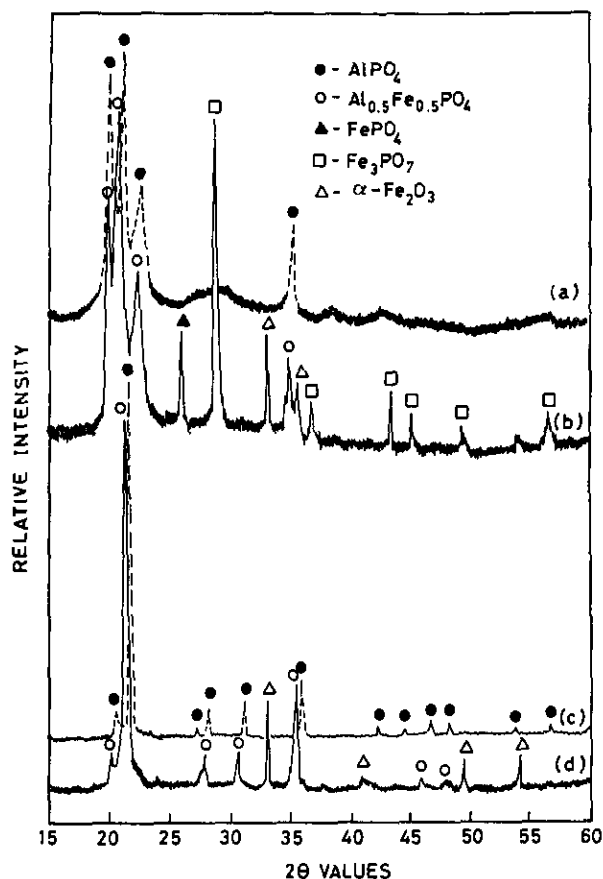
FIG. 5.   XRD pattern of the (a) tridymite form of $AlPO_4$, (b) tridymite form of $Al_{0.5}Fe_{0.5}PO_4$ (calcined at 1175 K), (c) orthorhombic form of $AlPO_4$, and (d) orthorhombic form of $Al_{0.5}Fe_{0.5}PO_4$ (calcined at 1325 K).

reduction in the distortion of oxygen anions around Fe^{3+}, thereby giving rise to an unresolved doublet.

The XRD patterns of $Al_{0.5}Fe_{0.5}PO_4$ calcined at various temperatures show that crystallization takes place at ≈ 975 K, and diffraction lines corresponding to the tridymite form of $AlPO_4$, the trigonal form of $FePO_4$, and Fe_3PO_7 are observed. The observed d values of the tridymite form of $AlPO_4$ indicate that at this temperature there is solid solution formation between $AlPO_4$ and $FePO_4$, although it is not complete. Further, due to limited solubility of $FePO_4$ in the $AlPO_4$ structure at this temperature, some $FePO_4$ has remained in the trigonal phase, which is decomposed to Fe_3PO_7 at this temperature of calcination. Up to a calcination temperature of 1175 K there is no phase transformation of the tridymite form (Fig. 5b). At $T \approx 1225$ K, the phase transformation has begun, and the diffraction pattern of the sample calcined at 1225 K shows both tridymite and orthorhombic phases along with α-Fe_2O_3. Further, the Fe_3PO_7 phase is absent due to its complete decomposition to the α-Fe_2O_3 form. At this stage the trigonal

form of $FePO_4$ is not observed due to complete incorporation in $AlPO_4$. Phase transformation is almost complete at a calcination temperature of 1325 K (Fig. 5d). This phase-transformation temperature is lower than that of pure $AlPO_4$. The lattice parameters of this orthorhombic phase are $a = 7.133$, $b = 7.216$, and $c = 7.154$ Å. These values show that the extent of the $FePO_4$ incorporation in the $AlPO_4$ lattice is certainly greater than that in the $Al_{0.75}Fe_{0.25}PO_4$ sample. [57]Fe Mössbauer spectra of $Al_{0.5}Fe_{0.5}PO_4$ samples calcined at various temperatures are shown in Fig. 6. The spectra shown in Figs. 6c, 6d, and 6e, corresponding to the mixed phosphates calcined at 975, 1075, and 1175 K, respectively, are fitted in three doublets corresponding to trigonal $FePO_4$, Fe_3PO_7, and the tridymite form of the mixed phosphate. Because of the high degree of overlap among these three quadrupole doublets, the consistency in the fitted values of δ and ΔEq, corresponding to the three spectra shown in Figs. 6c, 6d, and 6e, is slightly poor. The values of the isomeric shift and quadrupole splitting for the unreacted $FePO_4$ and Fe_3PO_7 are consistent with those obtained earlier from the analysis of the $FePO_4$ sample calcined at different temperatures. However, the values $\delta = 0.40 \pm 0.05$ mm/sec and $\Delta Eq = 0.45 \pm 0.05$ mm/sec corresponding to the tridymite phase are different from those obtained earlier, possibly because of the different composition of this sample. On calcination of the mixed phosphate at 1325 K the resolved quadrupole doublet of $FePO_4$ has changed to an unresolved quadrupole doublet ($\delta = 0.30$ mm/sec and $\Delta Eq = 0.27$ mm/sec), corresponding to the orthorhombic form of $AlPO_4$. This further confirms solid solution formation between $FePO_4$ and $AlPO_4$. The spectrum also shows a sextet along with the unresolved doublet due to α-Fe_2O_3 formation as observed in the XRD pattern. From the spectral area of the sextet and the unresolved doublet, the
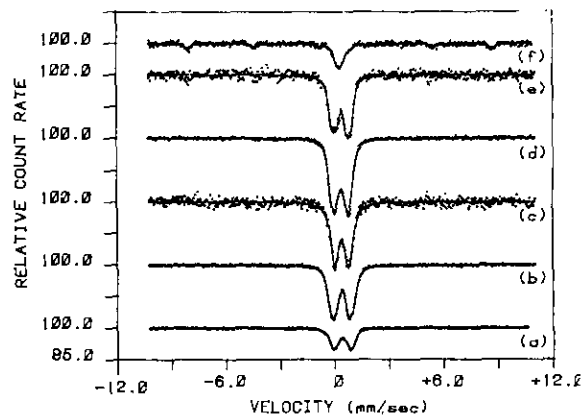

FIG. 6.   [57]Fe Mössbauer spectra of $Al_{0.5}Fe_{0.5}PO_4$ calcined for 20 hr at (a) 400 (oven dried), (b) 775, (c) 975, (d) 1075, (e) 1175, and (f) 1325 K.

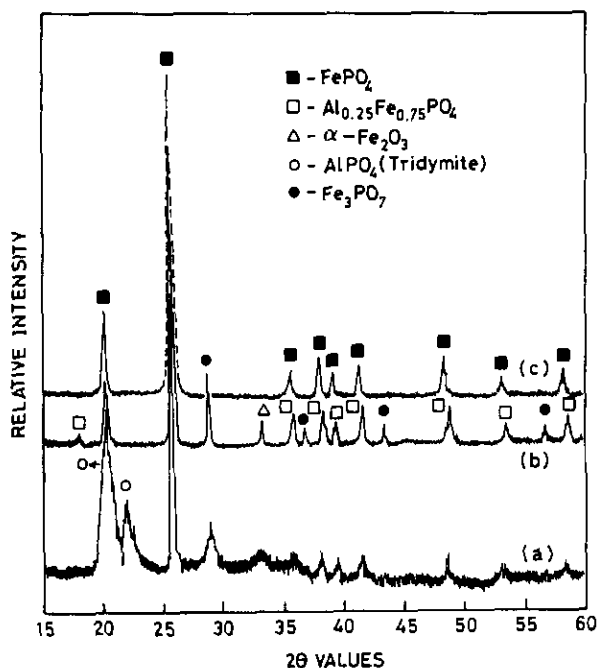FIG. 7. XRD patterns of Al$_{0.25}$Fe$_{0.75}$PO$_4$ calcined for 20 hr at (a) 975 and (b) 1075 K and (c) FePO$_4$ calcined at 875 K.

amount of FePO$_4$ incorporated is roughly calculated to be 0.33 of the initial concentration of iron in the Al$_{0.5}$Fe$_{0.5}$PO$_4$ composition.

The calcination behavior of Al$_{0.25}$Fe$_{0.75}$PO$_4$ samples shows that AlPO$_4$ crystallizes in the tridymite form at 875 K, whereas crystallization of FePO$_4$ takes place at 925 K. On calcination at 975 K FePO$_4$ has partially decomposed to Fe$_3$PO$_7$ (Fig. 7a). The tridymite phase of AlPO$_4$ remains as a separate phase up to a calcination temperature of 1025 K. At 1075 K complete incorporation of AlPO$_4$ into the FePO$_4$ lattice has taken place, and the calcined
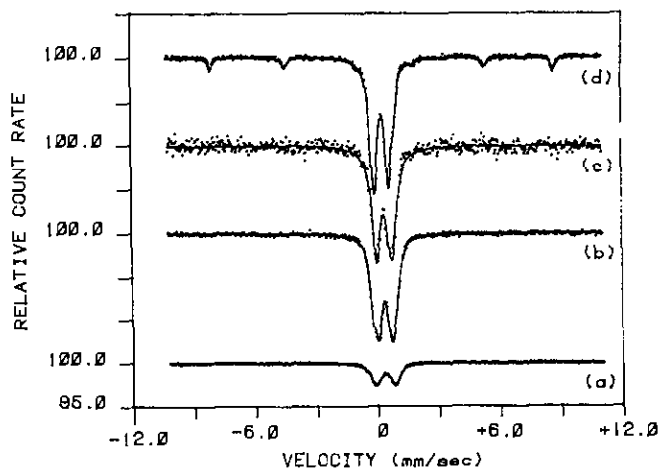

FIG. 8. ^{57}Fe Mössbauer spectra of Al$_{0.25}$Fe$_{0.75}$PO$_4$ calcined for 20 hr at (a) 400 (oven dried), (b) 775, (c) 975, and (d) 1075 K.

sample shows a XRD pattern similar to that of FePO$_4$ alone along with decomposition products of FePO$_4$ such as Fe$_3$PO$_7$ and α-Fe$_2$O$_3$ (Fig. 7b). This shows the formation of a solid solution between the two phosphates in a trigonal crystal structure similar to that of FePO$_4$. On solid solution formation the cell parameters show a slight decrease compared to those of FePO$_4$ (Figs. 7b and 7c). The observed lattice parameters are a = 5.010 and c = 11.130 Å compared to the lattice parameters a = 5.035 and c = 11.245 Å of pure FePO$_4$. ^{57}Fe Mössbauer spectra of Al$_{0.25}$Fe$_{0.75}$PO$_4$ calcined at various temperatures show no observable change in the FePO$_4$ spectrum due to solid solution formation with AlPO$_4$ (Fig. 8). The expected change in isomeric shift and quadrupole splitting arising due to crystallization of the sample has been observed.

CONCLUSIONS

In conclusion it can be said, based on the present studies, that although FePO$_4$ and AlPO$_4$ are not isostructural, it is possible to form their solid solution by coprecipitation of the constituent phosphates, followed by calcination at appropriate temperatures. In the Al$_{0.75}$Fe$_{0.25}$PO$_4$ composition, FePO$_4$ is stabilized and does not decompose due to its complete incorporation into the AlPO$_4$ lattice at about 975 K. The phase transformation of AlPO$_4$ also is affected and takes place at a lower temperature (T = 1075 K). Due to Fe^{3+} incorporation the lattice parameters of AlPO$_4$ are slightly increased for both the tridymite and the orthorhombic phase. The quadrupole splitting value of Fe^{3+} ions decreases from 0.45 to 0.25 mm/sec on transformation from the tridymite to the orthorhombic phase.

Similar results are obtained for the Al$_{0.5}$Fe$_{0.5}$PO$_4$ composition, but due to the higher temperature required for complete incorporation of FePO$_4$ into the AlPO$_4$ lattice, iron orthophosphate partially decomposes to Fe$_3$PO$_7$ and α-Fe$_2$O$_3$.

For the Al$_{0.25}$Fe$_{0.75}$PO$_4$ composition the incorporation of AlPO$_4$ into the FePO$_4$ structure takes place at ≈1075 K, and the trigonal structure of FePO$_4$ is retained. For this composition there is no observable change in the Mössbauer parameters of FePO$_4$ due to its solid solution formation with AlPO$_4$.

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