STUDY ON SYNTHESIS OF MAGNESIUM PHOSPHATE MATERIALS

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Keywords: Magnesium pyrophosphate, orthophosphate, XRD, DTA, TGA IR spectra.

Abstract: During preparation, the synthesis of magnesium pyrophosphate or orthophosphate is strongly affected by the nature of both starting materials and precipitating agents. Also the stoichiometry of reactants influences on the structure and composition of prepared samples. Several magnesium phosphate samples were prepared at room temperature as Mg₃(PO₄)₂.22H₂O, MgHPO₄.3H₂O NH₄MgPO₄.H₂O and NH₄MgPO₄.6H₂O. After calcinations of these samples at 850°C for 6h, MgHPO₄.3H₂O, NH₄MgPO₄.H₂O and NH₄MgPO₄.6H₂O were converted to pyrophosphates (α-Mg₂P₂O₇). But Mg₃(PO₄)₂.22H₂O converted to orthophosphate. The obtained solids were investigated as synthesized or after calcinations by various physicochemical techniques as X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). IR spectroscopy was used for only calcined samples.

(Received November 25 2009; Accepted February 4, 2010)

INTRODUCTION

Magnesium phosphates have many applications (1). They are used as bonding in refractors and mortars as rapid-setting cements and in various glasses. They also play an important role in catalysis, since they have found use in organic processes where acid-base surface properties are required (2-5). The chemical textural properties of phosphate materials depend on the particular synthetic procedure used. Thus, the properties of Al PO₄ vary with the preparation and thermal treatment method used (6) and also with the addition of urea, alkali ions (7) and sulfate (8) to the gelling medium. Altering the synthetic conditions can lead to different structures as shown in molybdenum phosphates (9). Various magnesium phosphates have been structurally studies in detail (10-13), however, with a few recent exceptions, they remain largely unexplored for catalytic purposes. The growing interest in catalytic uses for magnesium phosphate in highly relevant processes led us to undertake a comprehensive study on their synthesis and characterization. So the important factors which can affect on the structure and composition of the phosphate materials as the stoichiometry of reactants and nature of both starting materials and precipitating agents were studied.

EXPERIMENTAL

1. Solid synthesis

1.1. Reagents

Solids were prepared by gelling from various aqueous solutions of the reactants which included different Mg and P sources and diverse precipitants. Table (1) lists the synthetic variables studied. The precursor materials used in this work such as MgCl₂.6H₂O, MgSO₄.7H₂O, Mg (NO₃)₂.6H₂O, Mg (OH)₂, Mg₃(PO₄)₂.22H₂O, NH₄HPO₄ and (NH₄)₂HPO₄ were used without purification.

<table>
<thead>
<tr>
<th>Mg source</th>
<th>P Source</th>
<th>Precipitant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)₂</td>
<td>H₃PO₄</td>
<td>NaOH</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>(NH₄)₂HPO₄</td>
<td>NH₄OH</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>Na₂HPO₄</td>
<td></td>
</tr>
<tr>
<td>Mg(NO₃)₂</td>
<td></td>
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</table>

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1.2. Procedures

A. The effect of nature of the precipitating agent

A solution containing 0.1 mol of MgCl₂·6H₂O and 0.15 mol of H₃PO₄ in 500 ml of distilled water was prepared. The reactants were combined in stoichiometric Mg/P ratio = 3:2. The reaction was occurred in an ice bath under stirring, 3M of precipitating agent NaOH or NH₄OH was added drop wise until the PH = 9. The gel thus obtained was allowed to stand for 24h, filtered, washed with distilled water several times, air dried and calcined at 850°C for 6h. Several solids were prepared similarly, by using MgSO₄·7H₂O, Mg (NO₃)₂·6H₂O or Mg (OH)₂ as Mg source with H₃PO₄ as P source.

B. The effect of the nature of the starting materials

Some solids were prepared similarly as above by using MgCl₂, MgSO₄ or MgNO₃ as Mg source with different P sources such as (NH₄)₂HPO₄ and Na₂HPO₄. No precipitating agent was used and the stoichiometric Mg/P ratio was 1:1. The reactant addition sequences and experimental conditions were always the same.

C. The effect of the stoichiometry of reactants

Other phosphate solids were prepared by using Mg (OH)₂ as Mg source and H₃PO₄ as P source. No precipitating agent was used and the reactants were combined in two different stoichiometric Mg/P ratios 1:1 and 3:2, respectively.

All the obtained solids were filtered, washed several times with distilled water, air dried and calcined at 850°C for 6h.

2. Characterization

X-ray diffraction [XRD] patterns were recorded by using Brukur D8 advance diffractometer (Germany) using Cu Kα radiation. The obtained phases were compared with JCPDS tables. Infrared spectra for calcined solids were recorded over the wave number range 4000-400cm⁻¹ by using FTIR 300E Fourir Transform Infrared spectrometer. Thermovolumetric curves (TG and DTA) were obtained by using shimadzu DTA-50 and TGA-50 (Japan) between 50 and 1000°C with heating rate of 10°C/ min.

RESULTS AND DISCUSSION

1. XRD analysis

A. Effect of the nature of the precipitating agents

Depending on the nature of the precipitating agents, two samples of magnesium phosphates were prepared. The X-ray diffraction peaks of the two samples are illustrated in Fig. 1 and 2.

Figure 1 represents the X-ray diffraction patterns of the magnesium phosphate prepared by using NaOH as precipitant. For the uncalcined sample, the XRD patterns exhibit the formation of Mg₃(PO₄)₂·2H₂O according to the JCPDS (31-805). The formation of the hydrated magnesium phosphate due to the washing of the produced sample with water was observed by some authors (14). By calcinations of the produced hydrated sample at 850°C for 6hr, the sample converted to magnesium orthophosphate Mg₃(PO₄)₂ (JCPDS 33-876) and the hydrated water was lost.

On other hand by using NH₄OH solution as precipitant, the XRD patterns showed the formation of a mixture of ammonium magnesium phosphates having the chemical structure, NH₄MgPO₄·H₂O (Dittmarite) (JCPDS 36-1491) and NH₄MgPO₄·6H₂O (Struvite) (JCPDS 15-762) (Fig.2). After the calcinations at the same conditions as above these solids converted to magnesium pyrophosphate α-Mg₂P₂O₇ (JCPDS 32-626).

![FIGURE 1 XRD patterns of magnesium phosphate using NaOH as precipitant](image-url)
B. Effect of the starting precursors

By using Na$_2$HPO$_4$ and NH$_4$HPO$_4$ as sources of phosphates, the X-ray patterns (Fig. 3) of the produced samples showed the formation of single phases of MgHPO$_4$.3H$_2$O (Newberyites) (JCPDS 35-780) and NH$_4$MgPO$_4$.6H$_2$O, respectively. With calcinations all these prepared samples converted to pyrophosphate structure $\alpha$-Mg$_2$P$_2$O$_7$.

C. Effect of the Mg/P values

Generally, during the preparation of the magnesium materials, the stoichiometry is an important factor in the end product. In this work, when the ratio Mg/P=1:1, X-ray diffraction patterns (Fig. 4-a) showed the formation of MgHPO$_4$.3H$_2$O which lost the water of hydration to be converted to Mg$_2$P$_2$O$_7$ by calcinations, according to the following equations.

$$\text{Mg (OH)}_2 + \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{MgHPO}_4.3\text{H}_2\text{O}.$$  \hspace{1cm} (1)

$$2\text{MgHPO}_4.3\text{H}_2\text{O} \xrightarrow{850 ^\circ \text{C}} \text{Mg}_3\text{P}_2\text{O}_7 + 4\text{H}_2\text{O}$$ \hspace{1cm} (2)

When the Mg/P ratio change to 3:2 the presence of excess cations of Mg replace the hydrogen completely and led to formation of Mg$_6$(PO$_4$)$_2$.22H$_2$O (Fig. 4-b) which converted to magnesium orthophosphate by calcinations.

$$3\text{Mg(OH)}_2 + 2\text{H}_3\text{PO}_4 + 16\text{H}_2\text{O} \rightarrow \text{Mg}_6(\text{PO}_4)_2.22\text{H}_2\text{O}$$ \hspace{1cm} (3)

$$\text{Mg}_6(\text{PO}_4)_2.22\text{H}_2\text{O} \xrightarrow{850 ^\circ \text{C}} 3\text{Mg(PO}_4)_2 + 22\text{H}_2\text{O}$$ \hspace{1cm} (4)
FIGURE 4-b XRD patterns of magnesium phosphate with Mg/P =3:2.

FIGURE 5 IR spectra of magnesium orthophosphate and pyrophosphate.

2. FTIR spectoscopy

Figure 5 shows the IR spectra obtained for orthophosphate and pyrophosphate solids which calcined previously at 850°C for 6h. both spectra exhibit a very weak band at the region from 3000 to 3925cm⁻¹ due to OH group vibrations (15). A very weak band was also observed at the spectra of pyrophosphate and orthophosphate samples at 1520cm⁻¹ due to the formation of surface carbonates (16, 17). For spectra of only pyrophosphate sample, there was strong absorption in the 900-1300 cm⁻¹ range due to P-O stretching vibrations of pyrophosphate in all cases (2). Also for spectra of pyrophosphate, there were additional bands at 736, 587 and 555cm⁻¹. These bands can be ascribed to P-O-P vibrations (18, 19). For IR spectra of orthophosphate, a strong band was observed at 1098cm⁻¹. This band is present in all spectra of orthophosphates (20). Another band at 975cm⁻¹ is also associated with orthophosphates [M₃PO₄] (21). Additional bands at 745, 586 and 422cm⁻¹ have been assigned to different vibrations of phosphate ions (22).

3. Thermal analysis

To follow up the thermal behavior of the produced phosphates, the TGA and DTA behaviors were observed for three hydrated samples as sample (1) Mg₃(PO₄)₂.22H₂O, sample (II) NH₄MgPO₄.H₂O and NH₄MgPO₄.6H₂O and sample (III) MgHPO₄.3H₂O.

For sample (1) TGA curve (Fig. 6) exhibits total weight loss of 50% over the temperature range of 50-540°C corresponding to the loss of crystallization water in addition to water potentially adsorbed on its surface. The DTA curve for the same solid exhibits two endothermic peaks at 80°C corresponding to the loss of adsorbed water and at 420°C corresponding to conversion of Mg₃(PO₄)₂.22H₂O to anhydrous Mg₃(PO₄)₂(23). The appearance of an exothermic peak at about 700°C may attributed to the conversion of amorphous Mg₃(PO₄)₂ to crystalline form (24).

For sample (II), the TGA curve (Fig. 7) exhibits total mass loss amount to 36% corresponding to loss of residual ammonia and water from NH₄MgPO₄.H₂O and NH₄Mg PO₄.6H₂O structures in the temperature range 150-600°C(25). The DTA curve for this sample exhibits two endothermic peaks at the same range of temperature and an exothermic peak at 675°C attributed to the crystallization of amorphous α-Mg₂P₂O₇. For sample (III) the TGA curve (Fig.8) exhibits two weight loss steps between 120-250°C attributed to loss of 3mol. of H₂O and one mole of H with weight loss of 31.5%. The DTA curve for the same sample shows two endothermic peak at the same range of temperature corresponding to the loss of crystallization water and conversion of MgHPO₄.3H₂O to amorphous α-Mg₂P₂O₇. As sample (II), an additional exothermal peak occurred at 675°C which emphasized the crystallization of amorphous α-Mg₂P₂O₇ to crystalline form (24).
CONCLUSION

In this work, the obtained results indicated that, the synthesis of magnesium phosphates greatly depends on both starting materials and precipitating agents. The stoichiometry of reactants is also very important factor and can influence on the structure and composition of phosphate materials. X-ray results show that the pyrophosphates will be formed by calcinations of NH₄MgPO₄·H₂O, NH₄MgPO₄·6H₂O or MgHPO₄·3H₂O samples at 850°C. But MgPO₄·22H₂O sample will be converted to orthophosphate by calcinations at the same temperature. X-ray results were confirmed by IR spectra and DTA-TG results.

ACKNOWLEDGMENT

The author expresses sincere thanks to professor D. Stachel (Otto-Schott-Institute, Friedrich –Schiller University, Jena, Germany.), for her important contribution in this research subject.

REFERENCES