

Synthesis of magnesium titanates: comparative study between mechanical and coprecipitated mixtures

M.J. Martínez-Lope, M.P. Baura-Peña and M.E. García-Clavel

Centro de Ciencias Medioambientales del C.S.I.C., Serrano 115 dpdo., 28006 Madrid (Spain)

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Abstract

The formation of magnesium titanates from mechanical mixtures needed temperatures of calcination above 1000°C, whereas calcination of coprecipitated mixtures in the range 500–700°C allowed us to obtain these titanates.

INTRODUCTION

In previous papers [1–3] we gave some of the results obtained in a study of the coprecipitation from solutions of Ti(IV) and Mg(II) sulphates in different molar ratios by sodium hydroxide. Mixtures of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ were always obtained. Calcination of these mixtures in the range 500–700°C allowed us to obtain three magnesium titanates: MgTiO_3 , MgTi_2O_5 and Mg_2TiO_4 , depending on the molar ratio of Ti(IV) to Mg(II).

In this paper, we present a comparative study on the calcination of mechanical mixtures of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ in the molar ratios 1:1, 2:1 and 1:2 and coprecipitated mixtures from solutions of Ti(IV) and Mg(II) in the same molar ratios.

EXPERIMENTAL

Materials

The $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ was prepared in the laboratory according to ref. 4 (grain size 47–95 μm).

The $\text{Mg}(\text{OH})_2$ was obtained in the laboratory by precipitation with sodium hydroxide from an aqueous solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The precipitate was obtained by adding a concentrated aqueous solution of sodium hydroxide to the aqueous solution of magnesium sulphate. The solutions

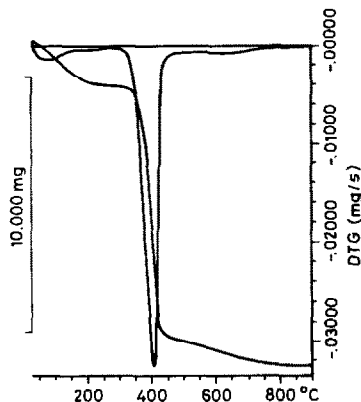


Fig. 1. TG and DTA curves (sample weight, 36.825 mg).

were stirred during the addition of the sodium hydroxide, and the pH was controlled using a pH meter. The precipitation of magnesium was complete at pH 12. The gelatinous white precipitate obtained was filtered off with a coarse (No. 4) glass filtering crucible.

In the filtrate, the magnesium content was analysed by complexometric titration with ethylenediaminetetraacetic acid (EDTA). The analysis was negative, indicating that precipitation was quantitative.

The precipitate was washed with cold distilled water to remove all sulphate ions. Atomic absorption was used to prove that the washed precipitate was free of sodium ions. The precipitate was dried at room temperature and ground (grain size 47–95 μm). The precipitate was identified by X-ray powder diffraction, thermogravimetry (TG) and differential thermal analysis (DTA).

The X-ray diagram of the precipitate corresponded to brucite, $\text{Mg}(\text{OH})_2$. Figure 1 gives the TG and DTA curves. In both curves, a small loss of water of humidity and, in the range 340–420°C, the dehydroxylation of $\text{Mg}(\text{OH})_2$ were observed. The X-ray diagram taken at 480°C showed the presence of MgO (periclase).

The thermal behaviour of $\text{Mg}(\text{OH})_2$ obtained from an aqueous solution of magnesium sulphate at room temperature or at the boiling point was identical.

Preparation of samples

Mechanical mixtures of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ($n = 1.1$) with $\text{Mg}(\text{OH})_2$ were prepared in the molar ratios 1:1, 1:2 and 2:1, using the precipitates obtained by us in the laboratory.

Coprecipitated mixtures in the same molar ratios as the mechanical mixtures were obtained by the procedure given in ref. 1.

Apparatus

Thermogravimetric analysis

A Mettler TA 3000 system with TG50 attachment was used at a heating rate of $600^{\circ}\text{C h}^{-1}$.

Differential thermal analysis

A laboratory-constructed system incorporating a vertical furnace and a temperature regulation system, both from Adamel, and a differential chromel–alumel thermocouple were used. The heating rate was $300^{\circ}\text{C h}^{-1}$.

X-ray powder diffraction

A Philips PW 1130 diffractometer was used, with a nickel filter and $\text{Cu K}\alpha_1$ radiation.

RESULTS AND DISCUSSION

Ti(IV):Mg(II) molar ratio 1:1

From the TG curves of the mechanical mixture and of the coprecipitated mixture, we obtained the curves of weight loss (%) as a function of temperature (Fig. 2). Curve a corresponds to the mechanical mixture and curve b to the coprecipitated mixture. The amounts of weight loss were calculated from the weights of the residue at 900°C ($\text{TiO}_2 + \text{MgO}$).

By comparing the two curves, we can observe that between room temperature and 300°C (zone of release of the humidity and water of hydration) curve b presents a greater weight loss than curve a.

In contrast, the dehydroxylation of brucite between 300 and 500°C represented in the mechanical mixture a weight loss of 15%. This loss is higher than that observed for the coprecipitated mixture (10%). The losses

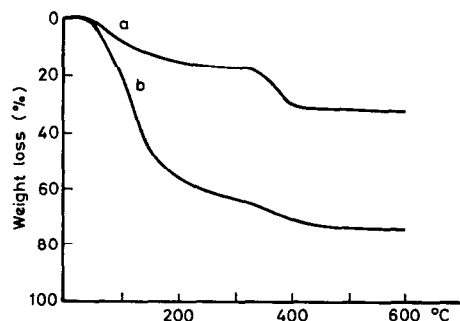


Fig. 2. Curves of weight loss (%) of the mechanical (curve a) and coprecipitated (curve b) mixtures (molar ratio 1:1).

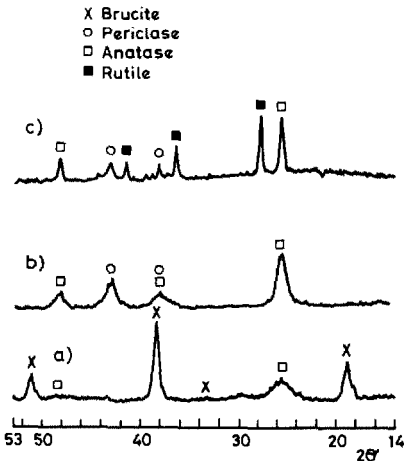


Fig. 3. X-ray diffraction patterns of the mechanical 1:1 molar mixture: curve a, at room temperature; curve b, at 450°C; curve c, at 700°C.

of water of hydration and of the hydroxyls overlap in curve b, while in curve a these losses are differentiated.

These results indicated that (i) the titanium in its precipitation carried down some of the magnesium present in the solution (specified as oxides, approximately 1 mol of MgO for every 3 mol of TiO_2), and (ii) 65–70% of the magnesium present in the solution was precipitated as $\text{Mg}(\text{OH})_2$.

The analysis by X-ray powder diffraction confirmed that the mechanical and coprecipitated mixtures were different.

The X-ray diagram of the mechanical mixture of $\text{TiO}_2 \cdot 1.1\text{H}_2\text{O}$ with $\text{Mg}(\text{OH})_2$ corresponded to brucite and poorly crystallized anatase (Fig. 3, curve a). The X-ray diagram of the coprecipitated mixture indicated that the precipitate was practically amorphous, and we could detect only an incipient order of the planes of brucite (Fig. 4, curve a').

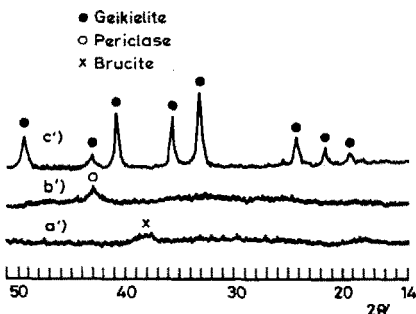


Fig. 4. X-ray diffraction patterns of the coprecipitated 1:1 molar mixture: curve a', at room temperature; curve b', at 450°C; curve c', at 700°C.

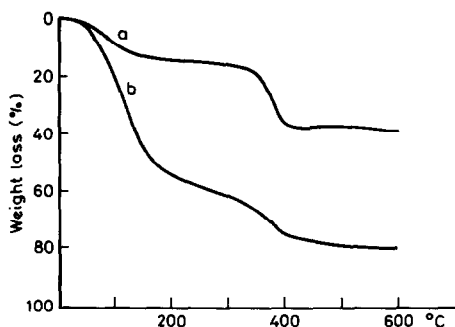


Fig. 5. Curves of weight loss (%) of the mechanical (curve a) and coprecipitated (curve b) mixtures (molar ratio 1:2).

The X-ray diagram of the mechanical mixture calcined at 450°C corresponded to a mixture of periclase and anatase ($\text{MgO} + \text{TiO}_2$) (Fig. 3, curve b). In contrast, the X-ray diagram of the coprecipitated mixture calcined at 450°C showed that the sample was practically amorphous, with slight evidence of periclase (Fig. 4, curve b').

The X-ray diagram of the mechanical mixture calcined at 700°C indicated a mixture of periclase (MgO), anatase (TiO_2) and rutile (TiO_2) (Fig. 3, curve c). The X-ray diagram of the coprecipitated mixture calcined at 700°C corresponded to geikielite, (MgTiO_3) (Fig. 4, curve c').

The X-ray diagram of the coprecipitated mixture calcined at 1000°C was identical to the diagram for calcination at 700°C. The X-ray diagram for the mechanical mixture calcined at 1000°C corresponded to periclase and rutile.

Ti(IV):Mg(II) molar ratio 1:2

Figure 5 shows the curves of weight loss (%) as a function of temperature. Curve a corresponds to the mechanical mixture and curve b to the coprecipitated mixture. Curve b presents between room temperature and 300°C a weight loss of about 62%; this value is similar to that for the coprecipitated mixture from $\text{Ti(IV):Mg(II)} 1:1$, which indicates that the titanium in its precipitation has carried away the same amount of magnesium as in the case of the equimolar mixture despite the amount of magnesium in solution being doubled. Therefore the weight loss due to the water of hydration is four times higher than in the mechanical mixture.

The weight loss due to the dehydroxylation of Mg(OH)_2 was higher in the mechanical mixture (22%) than in the coprecipitated mixture (17%). Thus 80% of the magnesium present in the solution is precipitated as Mg(OH)_2 .

The X-ray diagram of the mechanical mixture $\text{TiO}_2 \cdot 1.1\text{H}_2\text{O} : 2\text{Mg(OH)}_2$ (Fig. 6, curve a) showed a mixture of brucite and poorly crystallized

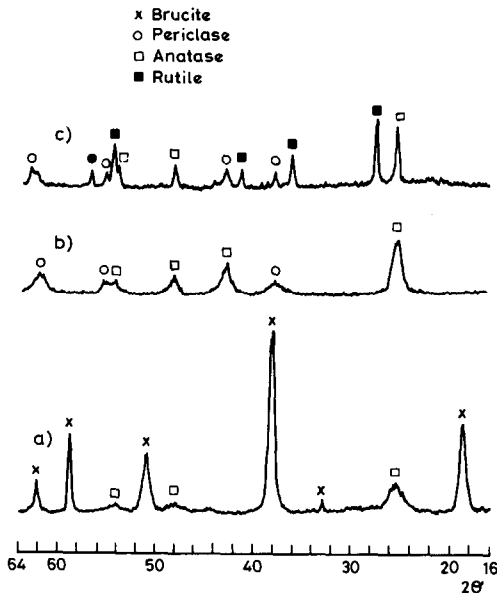


Fig. 6. X-ray diffraction patterns of the mechanical 1:2 molar mixture: curve a, at room temperature; curve b, at 500°C; curve c, at 700°C.

anatase. The X-ray diagram of the coprecipitated mixture indicated poorly crystallized brucite (Fig. 7, curve a').

When the dehydration was finished at 500°C, the X-ray diagrams of the residua from the two mixtures were different, as observed for the 1:1 molar mixtures.

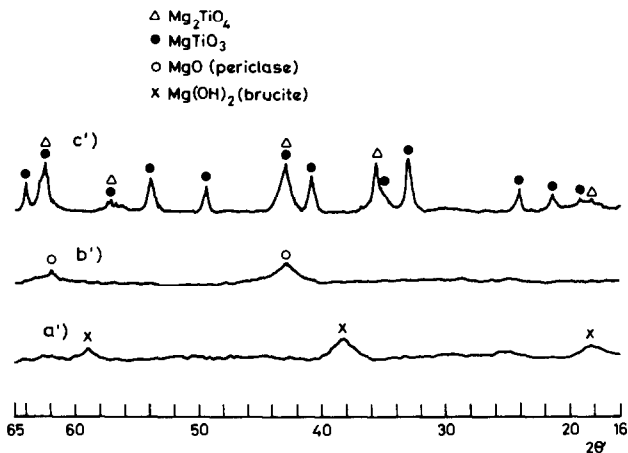


Fig. 7. X-ray diffraction patterns of the coprecipitated 1:2 molar mixture: curve a', at room temperature; curve b', at 500°C; curve c', at 700°C.

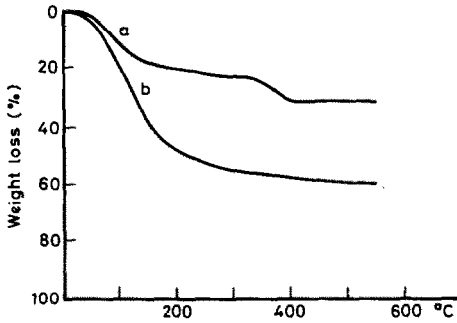


Fig. 8. Curves of weight loss (%) of the mechanical (curve a) and coprecipitated (curve b) mixtures (molar ratio 2:1).

The X-ray diagram of Fig. 6 (curve b) shows a mixture of periclase (MgO) and anatase (TiO_2), whereas the X-ray diagram of Fig. 7 (curve b') indicates poorly crystallized periclase.

The X-ray diagrams of the residues at 700°C for the two mixtures are shown in Figs. 6 and 7. The X-ray diagram of Fig. 6 (curve c) is identical with that of Fig. 3 (curve c). The X-ray diagram of Fig. 7 (curve c')

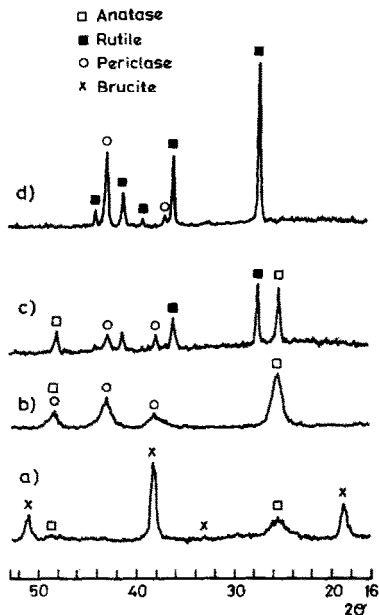


Fig. 9. X-ray diffraction patterns of the mechanical 2:1 molar mixture: curve a, at room temperature; curve b, at 450°C; curve c at 650°C; curve d, at 950°C.

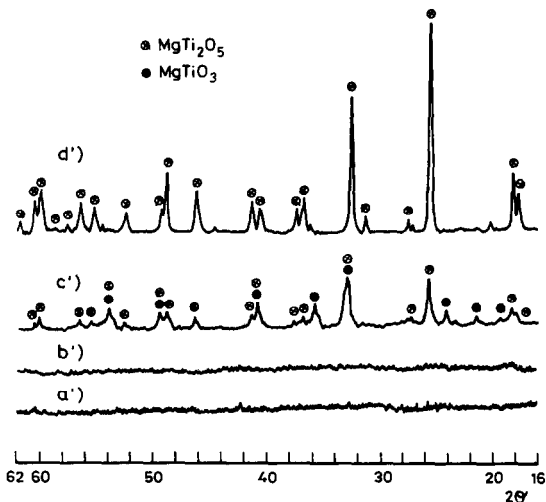


Fig. 10. X-ray diffraction patterns of the coprecipitated 2:1 molar mixture: curve a', at room temperature; curve b', at 450°C; curve c', at 650°C; curve d', at 950°C.

corresponds to magnesium orthotitanate (Mg_2TiO_4) and geikielite (MgTiO_3).

Ti(IV) : Mg(II) molar ratio 2 : 1

Figure 8 shows the curves of weight loss (%) as a function of temperature for the mechanical mixture (curve a) and the coprecipitated mixture (curve b).

Curve b shows only a weight loss; this indicates that all the magnesium has been precipitated with titanium.

Analysis by X-ray powder diffraction of the two mixtures showed that the thermal behaviour, as in the above-mentioned cases, was different.

The X-ray diagram of the mechanical mixture showed a mixture of brucite and poorly crystallized anatase (Fig. 9, curve a). The X-ray diagram of the coprecipitated mixture indicated an amorphous precipitate (Fig. 10, curve a').

The X-ray diagrams of the residua at 450°C of the two mixtures indicated a mixture of periclase and anatase (Fig. 9, curve b) and an amorphous precipitate (Fig. 10, curve b').

The X-ray diagrams of the mixtures calcined at 650°C showed a mixture of anatase, rutile and periclase (Fig. 9, curve c) and magnesium dititanate along with some low intensity lines of geikielite (Fig. 10, curve c').

Finally, the X-ray diagrams of the mixtures calcined at 950°C indicated a mixture of rutile and periclase (Fig. 9, curve d) and magnesium dititanate MgTi_2O_5 (Fig. 10, curve d').

CONCLUSIONS

The thermal behaviour of the mechanical and coprecipitated mixtures at temperatures below 1000°C was different.

In all the mechanical mixtures produced by heating a mixture of magnesium hydroxide and titanium oxide, the magnesium hydroxide and hydrated titanium oxide behaved in the same way thermally as when they were isolated. However, in the coprecipitated mixtures at temperatures below 1000°C, the formation of magnesium titanates took place.

These titanates were formed because, during the coprecipitation, a precipitate was obtained which was an intramicellar magnesium–titanium mixture and an intermicellar brucite–hydrated titanium oxide mixture. Consequently, the homogeneity of the mixture was more perfect than in the mechanical mixture.

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