Gelling Preparation of Starting Materials for Dry and Wet Syntheses of Silicate Minerals

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Abstract

Gelling technique on the preparation of starting materials of silicates for both dry and wet (hydrothermal) syntheses has been fundamentally reinvestigated on the following components, SiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, MgO, FeO, NiO and CaO by precipitating with excess ammonia water in ethyl alcohol solutions. On the basis of solubilities at each pH for each component, a general procedure for the preparation of starting materials including Na_2O and K_2O has been proposed.

1. Introduction

The ground glass method developed in the Geophysical Laboratory has been widely accepted in the field of dry synthesis of silicates, especially in the study of phase equilibria. However, this method is inconvenient, when the melting points of desired compositions are extremely high. Therefore finely pulverized oxide mixtures mechanically mixed have been conventionally used in this case. However, difficulties are often encountered owing to their sluggish reaction, sometimes accompanied with the formation of metastable phases. In order to prevent these difficulties "the nitrate calcination method" has been

Table 1 Chemicals available to present method.

Components	Chemicals	Analysis	
		Solubility	Standardization
SiO_2	Tetraethyl orthosilicate	Colorimetry	Gravimetry
Al_2O_3	Aluminum nitrate	EDTA	〃
Fe_2O_3	Ferric chloride	Atomic absorption	〃
Cr_2O_3	Chromium nitrate	〃	〃
MgO	Magnesium nitrate	EDTA	Gravimetry or EDTA
FeO	Ferrous chloride	Atomic absorption	Gravimetry
NiO	Nickel chloride	EDTA	Gravimetry or EDTA
CaO[†]	Calcium hydroxide	—	—
Na_2O[†]	Sodium carbonate	—	—
K_2O[†]	Pottasium carbonate	—	—

[†] Chemicals of JIS special grade or extra pure grade were used for each component. Mechanically blended later.

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employed mixing with silica sol or gel. On the contrary, another method of preparation so called "the coprecipitation method" has been developed. Roy[1] reported a method for both dry and hydrothermal studies using K– or Na–silicate as a source of SiO_2–component. However, these materials require electrodialyzation to eliminate absorped alkalies. This tedious work was improved later by Ito and Johnson[2], using resin. To avoid this difficulty "ludox", a kind of silica sol, has been widely accepted[3]. On the other hand, Roy[4] and Glasser and Osborn[5] developed "the alcoholic solution method", a variety of the coprecipitation method, instead of "aqueous solution method" in order to dilute tetraethyl orthosilicate, $Si(OC_2H_5)_4$, a new source of silica. Hamilton and Mackenzie[6], Hamilton and Henderson[7], and Bigger and O'Hara[8] carried out this method respectively in somewhat

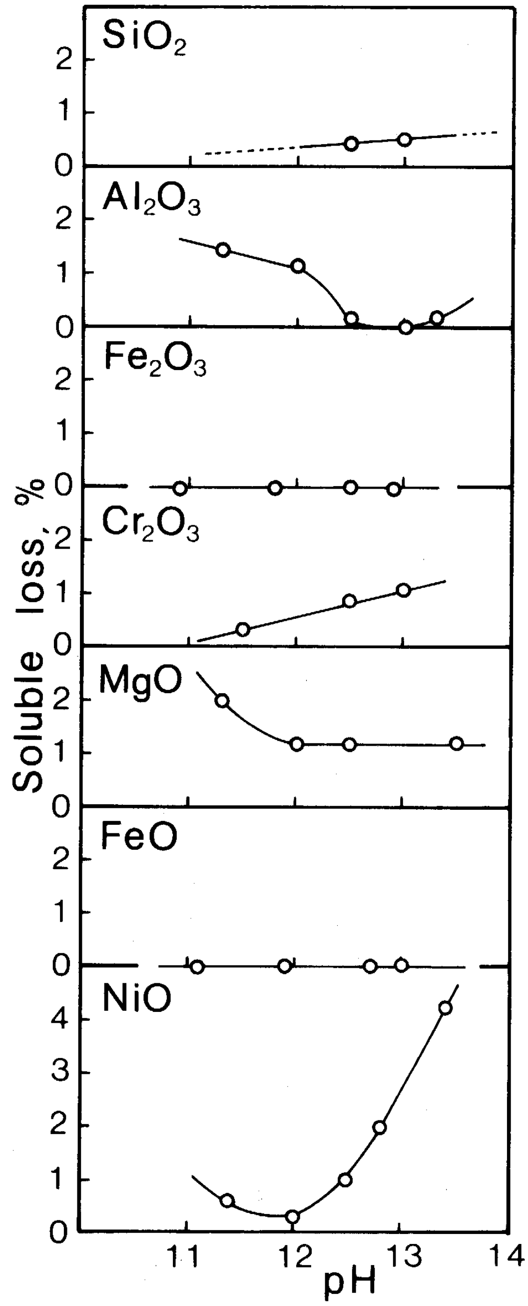

Fig. 1 Soluble loss of each component as a function of pH in alcohol–ammonia solution.

modified fashion. In this paper "the alcoholic solution method" will be reinvestigated widely to establish a better procedure on the preparation of starting materials for the synthesis of silicate minerals.

2. Experimental

Stock solutions of nitrate and chloride for each component listed in Table 1 were prepared, dissolving in ethyl alcohol* to show concentrations around 10 mg/ml and stored in airtight plastic bottles. It was found that ferric nitrate did not stand for long preservation, resulting muddy precipitates. The solubility of precipitates for each component was examined under various pH, poring ammonia water* to a 500 ml beaker containing aliquot quantity of stock solutions, 10–20 ml. After stirring, the beaker was placed on a water bath at 55℃ for 30 minutes. When the precipitates settled down, the pH was again adjusted with slight ammonia. The contents were filtrated after decantation and the residues were washed by alcohol several times. The filtrates were completely dried up on the water bath at 55℃ and precipitates after evaporation were dissolved completely by slight hydrochloric acid and diluted to a constant volume with deionized water to serve for next chemical analysis. The solubility of precipitates at various pH was determined by atomic absorption spectroscopy, EDTA titration or colorimetry. Conventional type of pH meter was employed.

3. Results and Discussion

Soluble loss of each component in alcohol–ammonia solution is represented in Fig. 1 with variation of pH. Generally, all components exhibit very low soluble loss except NiO–component whose soluble loss raises markedly at very high pH region. Both iron components, Fe_2O_3 and FeO have extremely low soluble loss, always nill irrespective of pH investigated. The soluble loss of Cr_2O_3–component increases slightly with increasing

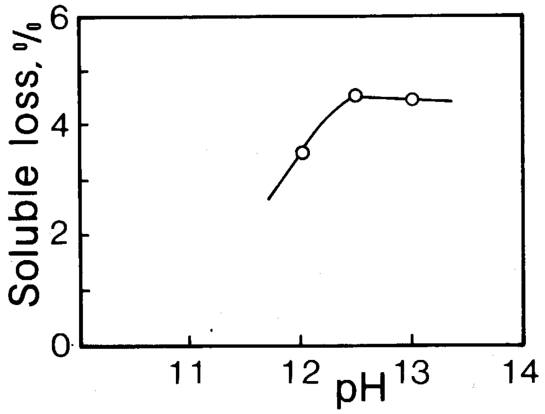

Fig. 2 Soluble loss of Ca–hydroxide as a function of pH in alcohol–ammonia solution in presence of ammonium nitrate.

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*JIS first grade.

pH and that of MgO–component becomes constant at high pH region, although its soluble loss is somewhat high. The Al_2O_3–component has a minimum and the soluble loss is rather small.

The hydrolysis of tetraethyl orthosilicate dose not proceed quickly at pH lower than 12.0 and the soluble loss of silica is very small at very high pH region. Consequently, if we intend to utilize these results for the preparation of gelling starting materials, the pH 12.5 should be selected where solubilities of precipitates are negligibly small throughout each component investigated.

On the other hand, however, there is an unpleasant problem ; that is the high solubility of CaO–component even at high pH region. To examine this, the solubility of the chemical, Ca $(OH)_2$ was tested in ethyl alcohol dissolving 0.1 M ammonium nitrate as initial concentration, assuming a practical operation. Results are given in Fig. 2 , showing rather high soluble loss. By this reason mainly, the methods ever reported have been obliged to dry gel mixtures or solutions up without filtration and to release forming ammonium salts and other volatiles by calcination, if CaO is one of the major constituents. The same procedure should be carried out, if alkalies are present.

4. Generalized Procedure as Conclusion

Prior to the preparation of gel mixtures, each stock solution should be standardized. Conventionally, gravimetric method is most suitable to aliquot quantity, 10–20 ml. The EDTA titration also will do to some components such as MgO– and NiO–components (Table 1). In latter case further dilution is required to accurate determination. For standardization of SiO_2–component, preaddition of suitable amount of standardized Fe_2O_3 stock solution is necessary to prevent silica gel from escape in the course of filtration. Rather rough determination of SiO_2–component is considered without analysis, only diluting adaquate volume or weight of tetraethyl orthosilicate with alcohol. However, the specific gravity of tetraethyl orthosilicate is generally smaller than that of pure one owing to the presence of some impurities.

Flow sheet of the general procedure for the preparation of gelling starting materials is given in Fig. 3. The components, CaO, Na_2O and K_2O should be mechanically blended later. This blending may give little influence on the reaction of starting mixtures, since these components secondary admixed are active enough.

Stock solutions are measured from a 25 ml burette in a 500 ml beaker to compose a desired mixing proportion. The total amount of mixing should be less than 5 grams in dehydrated state of coming precipitates. Then, ammonia water is pored slowly until the solution becomes pH 12.5, agitating continuously with a magnetic stirrer for a while and the beaker is transferred to a steam bath and the content is aged at 55℃ for 30 minutes. After setting of gelatinous precipitate, the pH is readjusted with ammonia. Then, the precipitate is recovered by means of filtration through 18.5 cm ϕ filter paper[*] . After washing the residue recovered in a funnel several times by alcohol[**], it should be air –

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[*] Toyo, No. 5B with medium porosity is suitable.

[**] This washing is very important to hydrothermal synthesis but not always necessary to dry synthesis.

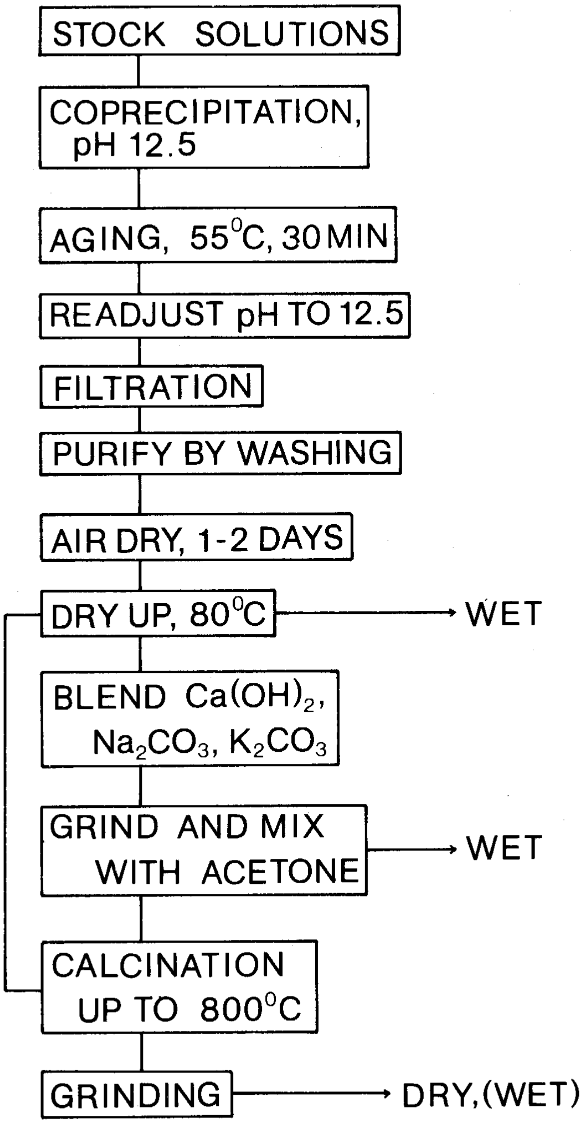

Fig. 3 Flow sheet of the procedure of gelling preparation. Outlets of wet and dry mean wet (hydrothermal) synthesis and dry synthesis, respectively.

dried for 1–2 days or more at room temperature holding in the funnel . Then the filter paper should be peeled from the funnel together with the residue. The half–dried cake is put into an evaporating dish together with the filter paper to dry completly on the steam bath at 80℃. The shrinked cake after drying should be removed carefully and entirely from the filter paper and transferred to an agate mortar. On this occasion crumpling and tapping the filter paper is helpful to recover adherent powders. Blending $Ca(OH)_2$, Na_2CO_3 or K_2CO_3 as CaO–, Na_2O– or K_2O–component, if necessary, futher mixing and grinding should be performed with acetone three times. An electric hair drier is conveniently used for the completion of drying. When the charge becomes stiff in the agate mortar, hot air from the dryer should be supplied carefully.* Although this powdered mixture enable directly to serve for hydrothermal synthesis, it should be gradually calcined up to 800℃ in Pt–crusible for dry synthesis, employing an electric furnace over-

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* Precaution should be paid. "Don't toutch the charge until it gets almost completely dry, or the charge will be blown away."

night. Without this heating treatment, great shrinkage and grain growth will occur in the course of the run at high temperatures.

This gelling technique will be widely applicable not only to the components studied in this paper but also to any oxide components whose salts are soluble in ethyl alcohol such as Ti–tetrabromide, Mn–nitrate, Sr–metal, Ba–bromide and so on, only checking their solubility at pH as high as 12.5. Some achievements have been gradually obtained by present method, especially in hydrothermal experiments[9),10)] In addition, urea may be available instead of ammonia at warmer condition of solution and this utilization can afford some spaces of investigation, since its mild dissociation brings slow increase of pH to get more homogenous precipitates.

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