Novel Syntheses of Inorganic Materials by Mechanochemical and Sonochemical Treatment(メカノケミカル及びソノケミカル処理による無機材料の合成)

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論文内容要旨

Chapter 1 Introduction

This work is a real challenge to discover new routes for preparing current technological materials by sophisticated techniques: These are mechanochemical and sonochemical routes by intensive grinding and irradiating ultrasound, respectively. The former route is mainly related to dry grinding and the latter to dispersed system in water basis. This thesis presents the fundamental investigations of novel mechanochemical and sonochemical techniques on the preparation of technological materials such as zinc ferrite ($ZnFe_2O_4$), tricalcium aluminum hydrate (C_3AH_6), $MgAl_2O_4$ spinel, hydroxyapatite (HAp), and zeolites (A and X types). All the processes start with the low-cost and widely available oxides and hydroxides as starting materials. Direct mechanochemical solid-phase reactions and dramatic decreases of reaction temperatures for the production of materials of unusual properties are successfully achieved through homogenizing fine grinding by energy-intensive grinding. The use of ultrasound can be also ensured as a new production route for fine ceramic powders and inorganic materials such as HAp and zeolite-A.

Chapter 2 Mechanochemical Synthesis of Zinc Ferrite from Zinc Oxide and Iron Oxide

This chapter discusses the direct mechanochemical synthesis of zinc ferrite ($ZnFe_2O_4$) from oxide powder mixture of ZnO and Fe_2O_3 by dry grinding at room temperature. The mechanochemical treatment results in the amorphization of starting substances at 2h of grinding, when most of them convert into amorphous Zn^{2+} and Fe^{3+} compounds and / or crystal $ZnFe_2O_4$. Nanosized $ZnFe_2O_4$ can be synthesized from the amorphous compounds at prolonged grinding for 3h. In this present oxide mixture, the direct mechanochemical solid-phase reaction for $ZnFe_2O_4$ is markedly enhanced when the amorphization of starting substances is progressed. Thermodynamic data ($\Delta G°_{298}$) and specific surface area (S_w) of the ground mixtures confirm the spontaneous reaction for $ZnFe_2O_4$ by room temperature grinding. Phase-pure $ZnFe_2O_4$ powder of high S_w can be produced by subsequent moderate calcination below 800℃. A HR-TEM microstructure of 3h-ground mixture reveals the formation of $ZnFe_2O_4$ from the amorphous compounds of starting substances.

Chapter 3 Mechanochemical Synthesis of Tricalcium Aluminum Hydrate from Calcium Hydroxide and Aluminum Hydroxide

This chapter deals with the non-stoichiometric mechanochemical solid-phase reaction for tricalcium aluminum hydrate (C_3AH_6) from the powder mixture of $Ca(OH)_2$ and γ-AlOOH by dry grinding at room temperature. Solid-phase reaction for C_3AH_6 from the powder mixture is greatly promoted when γ-AlOOH of inferior crystallinity is used than those of well crystalline. In this mixture system, the mechanochemical solid-phase reaction might be occurred through the amorphization followed by the dehydration of constituent solids. When the crystallinity of starting substances is inferior, therefore, dehydration processes induced by mechanochemical treatment are much improved. Formation of C_3AH_6 is improved as an increase in Ca/Al atomic ratio of starting mixture, however, the

time to be required for the preparation of C_3AH_6 in this non-stoichiometric powder mixture is retarded than that from the stoichiometric powder mixture. Prolonged mechanochemical treatment over 120min produces a more stable C_3AH_6 phase. Formation of its excess hydrates is enhanced in the presence of H_2O and free Ca, Al species.

Chapter 4 Synthesis of $MgAl_2O_4$ Spinel from Magnesium Hydroxide and Aluminum Hydroxide Activated by Grinding

This chapter investigates the novel mechanochemical method for preparing $MgAl_2O_4$ spinel precursor from the powder mixture of $Mg(OH)_2$ and $Al(OH)_3$ by dry grinding. The combined process of mechanochemical treatment and subsequent moderate calcination is proved to be an effective method for the production of very active spinel powder. The dry grinding promotes the dehydroxylation processes of starting substances, predominantly in $Al(OH)_3$ rather than $Mg(OH)_2$. Most of them readily convert into their amorphous compounds within 120min of grinding. Phase-pure $MgAl_2O_4$ spinel powders can be obtained by heating the precursor ground for 15min at the temperature as low as 900℃ for 1h. This combined process can be successfully adopted as the unique processing route for the preparation of spinel powder of high chemical homogeneity and sinterability. Relative density of sintered compact prepared from this combined route is 94% when the mixture is ground for 15min.

Chapter 5 Mechanochemical and Sonochemical Synthesis of Hydroxyapatite from Constituent Mixtures

This chapter proposes novel mechanochemical and sonochemical techniques for preparing hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) from constituent oxide and hydroxide mixtures of $Ca(OH)_2$-P_2O_5, CaO-$Ca(OH)_2$-P_2O_5, and $Ca(OH)_2$-H_3PO_4 with Ca/P atomic ratio of 1.67. Mechanochemical route can be well suited for the preparation of HAp monophase from these constituent mixtures. In the two powder mixtures, the preparation of HAp is much easier from the $Ca(OH)_2$-P_2O_5 mixture than the CaO-$Ca(OH)_2$-P_2O_5 one. From the former mixture, the mechanochemical solid-phase reaction for HAp is completed within 30min. Presence of free H_2O released during grinding plays a key role to promote these synthetic reactions. Especially in the former mixture, the grinding assists mechanochemical neutralization reaction of intermediate $CaHPO_42H_2O$ (DCPD) and $Ca(OH)_2$ to produce HAp favorably. In addition, sonochemical technique also promotes the formation of HAp monophase in $Ca(OH)_2$-H_3PO_4 suspension more effectively than conventional heating technique. Sonochemical processing for HAp from the present solid-liquid suspension results in complete synthetic reaction by 60min of sonicating. The use of ultrasound leads to the formation of very fine HAp powders with relatively narrow size distribution through dissolution and precipitation processes induced by intensive stirring.

Chapter 6 Synthesis of Zeolites from Kaolinite and Metakaolinite Activated by Grinding and Irradiating Ultrasound

This chapter investigates the effects of mechanochemical and sonochemical processing for zeolites production from kaolinite and metakaolinite in NaOH suspension. Dry and wet mechanochemical treatments combined by subsequent moderate heating can promote the synthetic reaction for zeolites from kaolinite. From this stimulating route, zeolite-A ($Na_{12}Al_{12}Si_{12}O_{48}27H_2O$) and zeolite-X ($Na_{20}Al_{20}Si_{24}O_{50}67H_2O$) can be prepared at the same time in the reactant solution at 60℃. Crystallization of zeolite-A and -X is largely dependent on the activated state of kaolinite so that the formation of zeolite-X is accelerated as activated state of kaolinite is improved. Also, the wet mechanochemical treatment modifies the composition of activated kaolinite. Rapid dissolution of AlO species from activated kaolinite is enhanced by wet milling together with NaOH to promote the formation of zeolite-X more effectively than zeolite-A. The rate of synthetic reaction for zeolite-A is improved by ultrasonic stimulation to metakaolinite-NaOH suspension. Ultrasonic stimulation route in the present heterogeneous reaction enables us to produce zeolite-A of very fine and relatively narrow-sized particles.

Chapter 7 Conclusion

Chapter 7 summarized the each chapter.

論文審査結果の要旨

省エネルギーと環境保全を考慮した少量多品種粉体製造プロセスの構築が望まれている。これに適合する手法として粉砕や超音波照射がある。これらの手法ではメカノケミカルないしソノケミカル効果が発現し、出発物質間での合成反応を促進するが、反応事例が不足しており、反応機構などに関する情報が必ずしも十分ではない。

本論文は、粉砕と超音波照射による無機材料からの機能性粉体の合成と、その反応機構を明確にしたものであり、全編７章よりなる。

第１章は、序論である。

第２章は、酸化亜鉛と酸化鉄を遊星ミルで乾式粉砕し、亜鉛フェライトを合成し、その反応機構を明確にしている。出発物質はミル処理時間の増大により微細化と無定形化が促進され、その進行過程で微小なフェライトの結晶核が生成し、成長することを明らかにした。

第３章は、消石灰とベーマイトの遊星ミルによる乾式粉砕から、カルシウム・アルミネート水和物（CAH）を合成し、反応機構を明らかにしている。粉砕過程では、出発物質双方が脱水反応を進行させて無定形化し、CAH 相の核が生成し、成長していくことを示した。また、ベーマイトの代わりに水酸化アルミニウムを用いる方が CAH が生成しやすくなることを示し、CAH 生成には出発物質の(OH)基の量が重要であることを明らかにした。

第４章は、水酸化マグネシウムと水酸化アルミニウムの遊星ミルによる乾式粉砕から、Mg-Al 系スピネルが合成でき、その反応機構を明らかにしている。スピネル生成反応は、粉砕による出発物質の脱水後、無定形化過程を経由して核生成と成長をたどり進行することを確認した。

第５章は、消石灰 - 五酸化リン、酸化カルシウム - 消石灰 - 五酸化リン、消石灰 - リン酸の３つの系に対し、遊星ミルによる乾式ならびに湿式粉砕の組み合わせと、乾式粉砕と超音波照射の組み合わせにより、それぞれヒドロキシアパタイト（HAｐ）を合成し、それらの反応機構を明らかにしている。乾式粉砕による HAｐの合成では、水分子が反応を支配する重要な因子であることを見出し、生石灰よりも消石灰を用いる方が有利であることを実証した。また、超音波照射は加熱法より短時間で HAｐが合成できることを明確にした。

第６章は、カオリナイトならびにメタカオリナイトを遊星ミルで乾式粉砕して機械的活性化した後、NaOH 溶液中で粉砕あるいは超音波照射し、加熱工程を経由するとゼオライトが常圧でも合成できることを明らかにした。これによってゼオライト - A 型と X 型が合成できるが、カオリナイトへの粉砕操作は、ゼオライト - X 型の選択的生成をもたらすことを見出した。また、メタカオリナイト - NaOH 系への超音波照射は、ゼオライト - A 型を生成しやすくすることを明確にした。

第７章は結論である。

以上要するに本論文は、粉砕と超音波照射という簡単な操作を固体や水相での固体分散系へ付与することによって少量多品種生産に即応した非加熱での機能性粉体合成を達成し、その反応機構を明確にしたものであり、地球工学、素材工学の発展に寄与するところ少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。