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号 |
発行年 | 1997
発行 | 

The synthesis of monodispersed particles perfectly controlled in size, shape and internal structure is essential to modern industries for the urgent demand of sophisticated particulate materials. Since most of monodispersed particles have been prepared in extremely dilute systems to avoid the tremendous coagulation, industrial production of such particles as ideal materials is confronted with the essential barrier of their exceedingly low productivity or high costs. A still more difficult issue is the systematic control of their average size, shape and internal structure on some definite guiding principles, and this has hardly been achieved in monodispersed particle systems. In this thesis, the methods for systematical control of the size, shape and structure of monodispersed hematite (α-Fe$_2$O$_3$) particles in the gel-sol systems have been established, and the mechanism of the shape and structure control of monodispersed α-Fe$_2$O$_3$ particles by sulfate ions has been studied. Moreover, Well-defined hematite particles have been analyzed by FTIR spectroscopy. This thesis is composed of five chapters. **Chapter 1** presents background, problems, objectives of this study, and an overview of this thesis. Since the properties of fine particles decisively depend on their size, shape and internal structure, the synthesis of monodispersed particles perfectly controlled in size, shape and internal structure is essential to modern industries for urgent demand of specific and sophisticated particulate materials, such as electromagnetic devices, ceramics, catalysts, photosensitive materials, pigments, etc. Also, the particles well controlled in size, shape and structure are ideal systems for basic research in the quantitative assessment of the properties of particles that are dependent on size, morphology and structure. It has been shown that anions such as chloride, hydroxide, sulfate and phosphate ions dramatically change the shape and internal structure of hematite particles. With respect to the mechanism of the shape and structure control few studies have been made. It is known that the infrared properties of fine particles are dependent on their size, shape and aggregation state. Some theoretical analyses have been made to explain those phenomena. However well-defined particles are needed for systematical studies.

This thesis presents in detail the newly established methods for systematic control of the size, shape, and structure of monodisperse hematite particles in the highly condensed gel-sol systems recently developed by Sugimoto et al. on the bases of the individual effects of temperature, seeding, and different kinds of anions. In addition, some new attempt to prepare uniform nanoparticles of α-Fe$_2$O$_3$ in large quantities are described. In particular, the mechanism of the shape and structure control by sulfate ions has been studied through investigation of the adsorption strength of sulfate ions to hematite surfaces of different crystal planes based on the sulfate adsorption isotherms, FTIR characterization of the structure of adsorbed sulfate ions on hematite surfaces, and UV analysis of
ferric complexes in the solution phase. The effects of the particle size, shape, internal structure and aggregation on the infrared absorptions are systematically analyzed using well-defined hematite particles perfectly controlled in size, shape and internal structure by the methods established in this thesis.

Chapter 2 describes various methods for systematical control of size, shape and internal structure of monodisperse \( \alpha-Fe_2O_3 \) particles on the basis of the gel-sol method recently developed by Sugimoto et al. The size could be controlled in the range from ca. 2 \( \mu \text{m} \) to ca. 0.3 \( \mu \text{m} \) without degrading the monodispersity by changing the temperature during the preparation of Fe(OH)\(_3\) gel or to ca. 30 nm by adding different amount of ultrafine \( \alpha-Fe_2O_3 \) seeds. The number of final hematite particles were found to be proportional to the number of added seeds. On the other hand, anions such as Cl\(^-\), OH\(^-\), SO\(_4^{2-}\), and PO\(_4^{3-}\) have remarkably different effects on the shape and internal structure. Chloride produced the pseudocubic shape by retarding the growth of the \{012\} faces. Sulfate and phosphate yielded the ellipsoidal or peanut-type particles by retarding the growth in the direction normal to the \( c \)-axis. The aspect ratio of the ellipsoidal particles was controlled from 1.1 to 5.2 by shape controllers such as sulfate and phosphate ions. The size of ellipsoidal particles can be controlled while the aspect ratio of the particles remains constant if we use fixed amount of shape controllers such as sulfate and phosphate, but add different amount of seeds. It was found at the same time that sulfate ions yielded polycrystalline particles consisting of much smaller subcrystals of a definite orientation, while phosphate produced nearly monocrystalline particles at a reduced concentration of chloride ions. Also, the decrease in concentration of chloride ions and elevation of aging temperature continuously increased the size of the subcrystals of each particle evaluated from the XRD peak broadening with the Scherrer equation. Finally, it has been shown that fairly uniform nanosized hematite particles can be prepared in large quantities as an application of a new technique for the preparation of the ultrafine \( \alpha-Fe_2O_3 \) seeds. As a result, it has become possible to control the mean size, shape, and internal structure of monodispersed hematite particles independently over a wide range.

Chapter 3 discusses the characteristics of the adsorption of sulfate ions to hematite particles to elucidate the anisotropic growth of hematite particles in the presence of sulfate ions. As expected, sulfate ions were found to be most strongly adsorbed to crystal faces parallel to the \( c \)-axis of the hexagonal crystal system from the adsorption isotherms of sulfate to hematite particles of different crystal habits, in accord with the retardation of their growth in the direction normal to the \( c \)-axis. It was found from FTIR spectroscopy that the adsorbed sulfate ions on the faces parallel to the \( c \)-axis, such as \{110\} and \{100\} faces, or on \{012\} faces took the bidentate structure to Fe ions on the surfaces, while monodentate structure was suggested for sulfate ions on the \( c \)-planes (\{001\} faces). The bridging-bidentate structure of adsorbed sulfate ions on those hematite surfaces may be elucidated in terms of the good matching between the O-O distance of a sulfate ion and Fe-Fe distance of these specific crystal faces. The adsorbed amount of sulfate ions to the \{012\} faces of hematite at 100°C decreased with increasing pH and became almost zero at pH ≥5, suggesting that the shape control with sulfate is possible only in the acidic media at pH ≤5. EDX and chemical analysis revealed that sulfate ions were rather uniformly incorporated into the ellipsoidal or peanut-type particles during their growth in the presence of sulfate ions. The adsorption of sulfate ions to hematite surfaces has been proved to be much weaker than phosphate ions, which accounts for the especially porous structure of the particles grown by the control of a relatively large amount of sulfate ions. On the other hand, sulfate ions in the solution phase with a high concentration of chloride ions such as 3.0 mol dm\(^{-3}\) were likely to be present in the form of free ions without forming a complex with Fe\(^{3+}\), as suggested from UV spectroscopy at 25°C. When the concentration of sulfate ions in the solution phase exceeded the level
for shape control of hematite, precipitation of acicular \( \alpha \)-FeOOH was observed. If hematite particles are present in such a system, \( \alpha \)-FeOOH was grown as whiskers on the hematite particles. When [SO₄²⁻] in the solution phase was higher than 0.1 mol dm⁻³, precipitation of basic ferric sulfate was also observed in addition to the growth of \( \alpha \)-FeOOH whiskers on hematite.

Chapter 4 discusses systematic FTIR analysis of well-defined \( \alpha \)-Fe₂O₃ particles varying in size, shape and internal structure. It has been found that the absorption peak frequencies of the pseudocubic particles are located between the corresponding theoretical peak frequencies of spheres and cubes and shift to lower frequencies as particle size increases, corresponding approximately with the Mie theory, but the peak shifts of single-crystalline particles are a little greater than the theoretical predictions probably due to the shape change from spheroidal to cuboidal pseudocubes with the size increase. However, the basic spectrum pattern was determined by the morphology of the particles. The observation on ellipsoids with various aspect ratios corresponded qualitatively with the theory on surface phonon modes in small particles, but revealed some essential discrepancies in the peak frequency between experiment and the theory, even if the particles were completely dispersed in the medium, probably due to the complex shape dependence of the depolarization factors rather than the aggregation effect. Thus effective depolarization factors were proposed and used in the theoretical treatment in order to improve the fitting between experiment and the theory. Peak frequencies of polycrystals are mainly determined by the size, morphology and overall directions of the crystal axes of a whole particle rather than those of each subcrystal. The subcrystal size mainly affects the peak width due to the intra-particle anharmonicity, which increases with the decreasing subcrystal size. Aggregation has some effect on the peak broadening in ordinary mixing procedure with matrix powder, but it can be avoided by complete mixing.

Chapter 5 summarizes the conclusions of the whole research work.
論文審査の結果の要旨

単分散微粒子はサイズ、形状、構造が均一であるため高い機能を有する先端素材であるが、従来より凝集防止のため希薄溶液系でのみ合成されており、工業的応用を考慮すると生産性の低さが実用化への強い障壁となっている。加えて、系統的なサイズ・形態・構造の制御法の研究は非常に少ない。本論文では、濃厚溶液系において、サイズ・形態などが均一な単分散微粒子の平均サイズ・形態・構造の系統的な精密制御法や、その機構について検討し、さらには、FT-IR 解析によるキャラクタリゼーションを行ったもので、全5章からなる。

第1章は、緒論であり、本研究の背景および目的を述べている。ここでは、従来の希薄溶液系からの単分散ヘマタイト微粒子群の生成機構に関する考察をまとめた上で、最近同研究室で開発された濃厚系における新合成法「グルーゾル法」の応用として、粒子のサイズ、形態、内部構造を精密に制御する方法、形態制御機構解明する手法、ならびに、FT-IR によるヘマタイト微粒子のキャラクタリゼーション手法を提案した。

第2章では、濃厚水酸化鉄ゲルからの単分散ヘマタイト粒子を合成する際、塩化物イオン、硫酸イオン、リン酸イオンの濃度を精密に制御し、かつ、超微粒子の種を共存させることにより、サイズ、形態、内部構造を系統的に制御する方法を開発したことを述べている。

第3章では、UV、FT-IR などの分析法を用いて、濃厚水酸化鉄ゲルから出発して単分散ヘマタイト粒子を合成する際の、硫酸根による形態制御機構の解明を行った結果について述べている。硫酸根はヘマタイト粒子の c 軸に平行な面に 2 点で強く吸着するが、c 面には弱い 1 点吸着をすることが分かった。このため、c 軸に垂直な方向の成長が阻害され、形態をエリプソイド型等に制御できることを明らかにした。

第4章では、単分散ヘマタイト微粒子のFT-IR解析に関して述べている。系統的なヘマタイト微粒子合成法の確立により、たとえば、同じ粒子体積で形や内部構造の異なる粒子群を生成させることができる。これら微粒子を用いて、サイズ、形態、内部構造のFT-IRスペクトラムへの影響を詳細に調べ、従来の理論を修正し、かつ、それら因子とスペクトル効果の関係を明らかにした。

第5章は結論である。

以上要するに本論文は、濃厚溶液系単分散ヘマタイト微粒子合成における、サイズ、形態、構造の戦略的な全く新しい精密制御手法を提案し、それを実証し、さらにその制御機構を解明するため、資源素材工学、コロイド化学ならびに関連する工業の発展に寄与するところが少なくない。

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。