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Multi-component and multi-phase population balance model: The case of Georgeite formation as methanol catalyst precursor phase



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HIGHLIGHTS

- Model for classification of precipitations systems into components and solid phases.
- Application to industrial relevant formation of catalyst precursors in a T-mixer.
- Reaction controlled catalyst precursor formation in T-mixer and simulations.

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ABSTRACT

A novel generally applicable multi-component and multi-phase population balance model is presented. The model classifies precipitation and crystallization systems into the number of components (i.e. building units of solid) and number of solid phases. The model includes reaction equilibria of metal ions in aqueous media, activity modeling, mixing, particle formation kinetics, population and mole balances. The new model is applied to the initial stages of copper catalyst precursor formation. The population balance model is simplified to a single-solid phase and multi-component precipitation. Simulations for several solid phases were performed at various experimental conditions. We show that the formation of the carbonate rich Georgeite phase is favored. The simulation results are verified by the measured global parameters pH and solid weight. Mixing plays a minor role in comparison to the variation of the reactant concentration. The timescale of precipitation including mixing, nucleation and crystal growth ranges from microseconds up to 1 s depending on the extent of secondary nucleation.

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1. Introduction

Modeling and simulation of reactive crystallization is so far mostly restricted to one component systems like zinc oxide (Segets et al., 2012) and L-glutamic acid (Cornel et al., 2009) or simple two component model systems like barium sulfate (Schwarzer and Peukert, 2004) and calcium carbonate (Kralj et al., 1990). However, many industrial processes are usually much more complex due to their multi-component and multi-phase character. Often several reactants which contain more than one component in the solvent are used as feed for the synthesis. Hence, potentially more than one solid phase of varying composition in terms of components can form (multi-component and multi-phase). This applies, for instance, for well-established co-precipitation methods

for catalyst synthesis (Deutschmann et al., 2000). Also in nanotechnology the trend goes towards ternary and higher component systems. Examples are copper indium sulfides (Yu et al., 2013) or even four component kesterite ($\text{Cu}_2\text{ZnSnS}_4$) phases (Ahmad et al., 2013) with unique optical and electronic properties, cobalt ferrites (Chinnasamy et al., 2002) for magnetic properties or LiFePO_4 (Park et al., 2004) for battery materials. Therefore, a considerable demand of a general model exists which should include components and solid phases without any restriction of their number. In this work we propose a novel multi-component and multi-phase population balance model which is able to track the transient particle formation of such complex particles.

The model is applied to the precursor formation during methanol catalyst synthesis whereby the word precursor refers to the initial precipitate. In industry a ternary calcined $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst is used for the large-scale production of methanol. The industrial manufacturing of the catalyst is carried out in the following steps: precipitation of metal salts in aqueous phase,

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aging in a stirred vessel, washing, drying, calcination and pelleting (Bems et al., 2003). Beside the particle size the composition of the product controls its properties and quality. The zinc substituted malachite solid phase as an aging product is favored which is known to result in a highly active calcined catalyst (Baltes et al., 2008). Therefore, it is mandatory to understand the physical and chemical backgrounds particularly in the first steps of solid formation where the final catalyst structure is predetermined.

This paper aims to model the primary Cu-system only. However, already six components ($\text{Cu}^{2+}/\text{NO}_3^-/\text{Na}^+/\text{CO}_3^{2-}/\text{H}^+/\text{H}_2\text{O}$) and three solid phases (copper hydroxide $\text{Cu}(\text{OH})_2$, Gerhardtite $\text{Cu}_2\text{NO}_3(\text{OH})_3$ and Georgeite) with the composition of crystalline Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$ are taken into account.

In the first part of this work the multi-component and multi-phase model is introduced. In the second part the model is applied and simplified to the formation of initial precipitates by hydrolysis of the copper component with underlying kinetics from the classical nucleation theory and diffusion-limited growth. The precursors' composition is taken into account by nanoparticle formation of the three known copper minerals. For each mineral a single-phase and multi-component simulations are performed. The particle formation of different mineral phases under standard conditions of catalyst formation and the influences of reactant concentrations, secondary nucleation and mixing on precipitation are discussed by parameter studies.

2. Model

2.1. Multi-component and multi-phase classification of crystallization and precipitation systems

The case of methanol catalyst precursor precipitation in this work as well as many other precipitation and crystallization systems can be classified in terms of multi-components and multi-phases. First of all it is important to distinguish between components and species. Morell and Hering (1993) defined components as “a set of chemical entities that permits a complete description of the stoichiometry of a system”. Species include sets of free ions and complexes. Especially in aqueous systems many complexes occur such as metal hydroxides. Complexes consist of a combination of free ions, e.g. metal cations and free hydroxide. Hence, usually free ions are chosen as components and all complexes are uniquely described by the combination of free ions.

For example the complex $\text{Cu}(\text{OH})^+$ can be expressed by the two components Cu^{2+} and OH^- . In principle, all species can be chosen as components including the complex $\text{Cu}(\text{OH})^+$. By further choosing OH^- as a component, the free ion Cu^{2+} can be expressed by the two components $\text{Cu}(\text{OH})^+$ and OH^- . Thus, the total number of components remains the same and is unique for the particular system independent from the choice of components.

To demonstrate the concept of multi-components and multi-phases, a map with the number of solid phases N_i and components N_p is shown in Fig. 1 in which four systems from literature and the system in this study are exemplarily included. For visualization the number of solid phases N_i is plotted against the components' number N_p which accounts for all components in the reactant solutions

The simplest system in terms of number of components and solid phases is the zinc oxide (ZnO) quantum dot system. The synthesis is performed by lithium hydroxide addition to a ZnO precursor dissolved in ethanol. So far, the dissociation of lithium in ethanol is not included in the model of Segets et al. (2012) reducing the ZnO formation to a transition of the ZnO precursor phase (as single component $N_p = 1$) to the ZnO nuclei (as single solid phase $N_i = 1$). The single solid phase ($N_i = 1$) barium sulfate

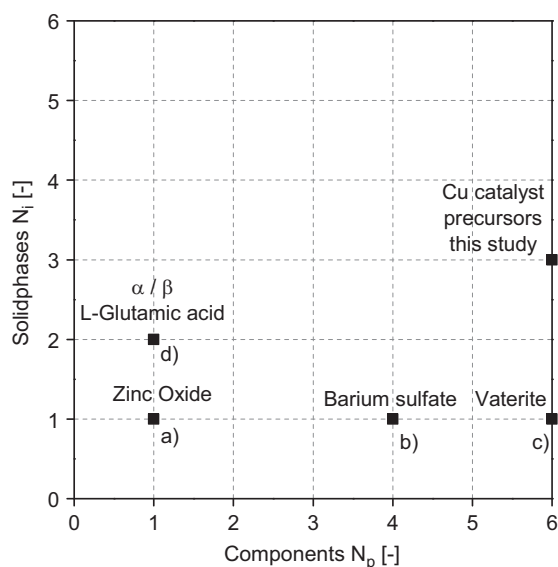


Fig. 1. Classification of different crystallization and precipitation systems into components and solid phases; (a) Segets et al. (2012) (b) Schwarzer and Peukert (2004) (c) Kralj et al. (1990) (d) Cornel et al. (2009).

system which is mentioned in the introduction includes four components ($N_p = 4$; Ba^{2+} , SO_4^{2-} , Cl^- , and H^+) by using barium chloride and sulfuric acid as reactants (Schwarzer and Peukert, 2004). The precipitation of the calcium carbonate polymorph Vaterite is induced by reacting solutions of calcium chloride and sodium carbonate. For adjusting the pH and the ionic strength sodium hydroxide, hydrochloric acid and sodium chloride are used (Kralj et al., 1990). This results in total six components ($N_p = 6$; Ca^{2+} , Cl^- , Na^+ , CO_3^{2-} , H^+ , and H_2O) and one Vaterite solid phase ($N_i = 1$). In this case water is included as component because it is essential to model the dissociation of the involved acid and bases in aqueous media. An extraordinary case is the crystallization of L-Glutamic acid from one component in the reactant solution which can result in two polymorphs (α and β). For each polymorph Cornel et al. (2009) set up one population balance equation. Hence, this system can be classified in two solid phases ($N_i = 2$) and one component ($N_p = 1$).

The case of the methanol catalyst precursor precipitation with three solid phases and six components can be found in the right upper corner in Fig. 1 which indicates the complexity of this particular system. For the presented systems in Fig. 1, well-established models already exist in literature. However, in future, this concept can help to identify components and solid phases for other precipitation and crystallization systems. It is the starting point to apply the model equations in the next sections and to create a model for the particular system of interest.

2.2. Mole balance

The integral mole balance is the central balance equation in this work.

$$\frac{Dn_p}{Dt} = \int_{A(t)} (\vec{j}_p) dA + \int_{V(t)} (B_p - D_p) dV \quad (1)$$

It is derived from continuum mechanics and describes the balance of the amount n_p of each component p in units of mol in a balance volume $V(t)$. The temporal change of the component's amount n_p (left hand side Eq. (1)) is influenced by the exchange of component p through the surface of the balance volume $A(t)$ (first term, right hand side of Eq. (1)) and the inner change of component p by source B_p and sink D_p rates (second term, right hand side of Eq.

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