



Synthesis of nickel oxalate particles in the confined internal droplets of W/O emulsions and in systems without space confinement

Bina Sengupta, Chirag A. Tamboli, Ranjan Sengupta*

Chemical Engineering Department, The Maharaja Sayajirao University of Baroda, Vadodara 390 001, India

ARTICLE INFO

Article history:

Received 29 November 2010

Received in revised form 28 February 2011

Accepted 5 March 2011

Keywords:

Nickel oxalate

Emulsion liquid membranes

Precipitation stripping

Particle size distribution

Aggregation

Cluster formation

ABSTRACT

Nickel oxalate particles were synthesized in the confined internal aqueous phase droplets of water in oil (W/O) emulsions using the emulsion liquid membrane (ELM) system, with D2EHPA as the carrier and oxalic acid solution as the precipitating agent. The effect of parameters such as carrier concentration, mole ratio of nickel to oxalic acid and internal phase volume fraction of the emulsion on the rate of nickel uptake, characteristics of particles formed, their morphology and particle size distribution was investigated. Nickel oxalate particles were also synthesized in systems where confinement of space did not exist, such as the precipitation stripping (PS) technique and in homogenous solutions, under conditions similar as that in the ELM systems. Particles obtained in ELMs differed from particles obtained by other techniques in morphology and size. Evidence of cluster formation by diffusion limited aggregation and cluster–cluster aggregation was observed. Particle sizes of nickel oxalate synthesized in the confined space of water droplets in ELM systems were smaller by one order of magnitude in comparison with the other two methods. The mechanism of spheroid cluster formation by fast precipitation is elucidated. Controlled calcinations of the nickel oxalate particles yielded the commercially important nickel oxide particles that were granular in nature and porous in structure. The ELM and PS techniques provide technological options of recovering nickel from dilute waste streams and obtaining the commercially important oxide.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Nickel oxalate is widely used for the synthesis of the commercially important nickel oxide which is obtained by the controlled decomposition of the oxalate. Nickel oxide is one of the few oxides that exhibit p-type semi conductivity and can be used as a transparent semiconducting layer. Gold doped nickel oxide films can be used as transparent electrodes in optoelectronic devices. Nickel oxide also exhibits anodic electrochromism and is being studied for application in smart windows [1], electrochemical super capacitors [2,3] and dye sensitized photo cathodes [4]. It is also used for making electrical ceramics, pigments for ceramic, glasses and glazes.

Nickel oxide has been synthesized by many different methods such as evaporation, spluttering, electro deposition, and sol–gel technique. Recently Salavati-Niasari et al. [5] synthesized nickel oxide nanoclusters via thermal decomposition of nickel oxalate precursor. The particle size of the nanoclusters was controlled by the presence of surfactants oleylamine and triphenyl phosphine

in the reaction system. These investigators have also synthesized nickel oxide nanoparticles via heat treatment of nickel octanoate precursor [6].

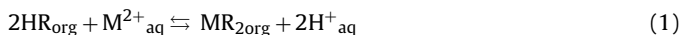
Out of the different routes for the synthesis of nickel oxide the two step process, involving the formation of nickel oxalate and its subsequent thermal decomposition to the oxide, appears to be the simplest and most viable for large scale applications. Nickel oxalate has been synthesized using a variety of solution processes such as precipitation from homogenous solutions [7–10], the sol–gel method [11], and the reverse micellar route [12]. Oxalate particles have also been precipitated in the confined space of the internal droplets of W/O emulsions using the emulsion liquid membrane (ELM) technique [13–15]. However, attempts to synthesize nickel oxalate in ELM systems was not encouraging due to the low yield of oxalate formed [16].

An ELM system involves the preparation of a W/O emulsion and dispersing the same in a feed solution containing the solute. The oil phase of the emulsion is the liquid membrane that separates the aqueous feed phase from the internal water phase of the emulsion. When dispersed the emulsion breaks down into tiny globules of 0.5–3 mm in diameter and within each globule exists a multitude of stagnant aqueous phase droplets containing the stripping reagent having sizes ranging from 0.3 μm to 10 μm. A metal extractant (carrier) is added to the membrane phase to transport metal ions from

* Corresponding author. Fax: +91 0265 2423898.

E-mail addresses: bina.msu@yahoo.co.in (B. Sengupta), ranjan.msu@yahoo.co.in (R. Sengupta).

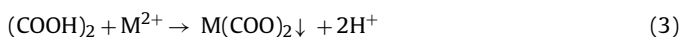
the feed to the internal aqueous phase of the emulsion. The metal ions in the feed react with the carrier (HR_{org}) at the external interface between the emulsion globule and the feed as described by Eq. (1)



The resulting metal–carrier complex (MR_{2org}) diffuses through the oil membrane phase of the emulsion and on contact with the acidic stripping phase of the emulsion at the internal interface between the membrane and internal aqueous phase droplets gets stripped of the metal as per Eq. (2).



The stripped carrier shuttles back to the feed interface to bind with metal ions in the feed to transport them to the internal phase of the emulsion. When oxalic acid is the stripping agent, precipitation of the sparingly soluble metal oxalates takes place within the confined space of the internal droplets as fine particles as per the overall reaction (3)



The precipitation stripping (PS) technique is a two stage process, where the metal ions from an aqueous feed is loaded in an organic solvent containing the metal extractant in the first stage as per Eq. (1) and subsequently in the second stage the solvent is stripped of the metal ions by contacting with suitable stripping agents as per Eq. (3), which results in the precipitation of a metal salt in the stripping phase. The major difference between an ELM system and PS system stems from the fact that in an ELM system the particles get synthesized in the confined space of stagnant stripping phase droplets within the emulsion globules while in PS systems there is no such space confinement and the stripping phase is in agitated state.

Conventional precipitation processes in homogenous solutions involve five stages: solution purification, precipitation, solid liquid separation and washing, classification and comminution. When the particle precursors are in dilute solutions, an additional pre-concentration step is necessary in conjunction with the solution purification stages. In comparison with this, precipitation in ELM system as well the PS system eliminates the pre-concentration and purification step of the precursor solution because the presence of the carrier induces specificity and selectivity to the process [13].

In the present investigation nickel oxalate particles were precipitated in the confined internal droplets of W/O emulsion using the ELM technique with D2EHPA as the carrier. Effect of parameters such as mole ratio of nickel to oxalic acid in the system (M), extractant concentration (C_e), internal phase volume fraction (ϕ) and nickel salt precursors on the nickel uptake by the emulsion as well as on the material characteristics of the particles formed were investigated. Nickel oxalate particles were also synthesized by the precipitation stripping (PS) technique and in homogenous solutions. The total moles of reactants in the system and the mole ratio of nickel to oxalic acid was kept identical in the three synthesis techniques investigated and the particle size distribution and morphology of the particles obtained by these three methods were compared and the plausible growth mechanism elucidated. Eventually nickel oxide particles were obtained from the nickel oxalate particles by calcinations under controlled conditions.

2. Experimental

2.1. Materials

D2EHPA {Bis(2-ethylhexyl phosphoric acid)} supplied by Fluka was used as the extractant. Span 80 (Sorbitan monooleate) supplied

by S. D. Fine Chemicals was the emulsifier. Kerosene (Indian Oil Corp. Ltd.) having boiling range 152–271 °C containing n-paraffins (27.08%), naphthenes (55.92%), aromatics (16%) and olefins (1%) having density (ρ_{15}) of 821.3 kg/m³ was used as the membrane material. The extractant, kerosene and the emulsifier were used directly as received from the manufacturers. The nickel salts (AR grade), nickel nitrate, nickel chloride and nickel sulfate all as hexa hydrates were procured from Merck Specialties Limited. All other reagents used were also of AR grade.

2.2. Emulsion preparation and characterization

The W/O emulsions were prepared by blending kerosene (membrane phase), D2EHPA (0.1–10%, v/v of the membrane phase) and emulsifier Span 80 (5%, wt/wt of membrane phase) with an aqueous solution of oxalic acid using a high-speed blender at 12,000 rpm. The volume fraction of the internal phase was 0.5 except when the internal phase volume fraction was varied. The resulting milky white W/O emulsion was cured for 30 min prior to dispersion in the feed phase.

Brookfield cone and plate Rheometer model (LV DV III + CP) was used to determine the viscosity of the emulsions using cone spindle CPE 52. The internal drop sizes of the emulsion were measured microscopically using Olympus microscope model BH-2 attached with an Olympus photo micrographic system model PM-10 AD at a magnification of 600×. The Sauter mean diameter was calculated for each case based on the measurement of more than 1000 droplet sizes as discussed in our earlier paper [17].

2.3. Nickel extraction and nickel oxalate particle synthesis

Extraction of nickel was carried out at 30 ± 1 °C in a four baffled batch extractor 0.105 m in diameter equipped with a six bladed disk turbine agitator having disk diameter 0.038 m. Raghuraman et al. [18] reported that nickel shows fairly good extraction from aqueous phase containing acetate buffers in the pH range 4–5. Zielinski et al. [19] investigated the precipitation stripping of nickel and other bivalent cations with oxalic acid from loaded oil phases containing D2EHPA as the carrier. They showed that oxalic acid solutions could precipitate metals in one-stage operation with efficiencies over 90%. Oxalic acid solution concentration of 30 g/dm³ was found suitable for nickel precipitation and stripping. Hence, feed containing the nickel precursor was maintained at a pH of 4.6 using an acetic acid–acetate buffer and the oxalic acid concentration was varied in the range of 0.05–0.26 M. The emulsion to feed ratio was maintained at 1:6 by adding 100 ml of cured emulsion to 600 ml of the feed solution. Uniform dispersion of the emulsion in the feed phase was obtained by stirring the contents at 160 rpm. Samples from the feed phase were withdrawn at definite time intervals and analyzed for nickel concentration using atomic absorption spectrometer (Chemito AA 203) at 231.92 nm. On completion of the extraction run the emulsion was separated from the feed phase washed with water and subsequently demulsified using acetone. The particles synthesized in the internal phase of the W/O emulsion were separated by centrifugation, washed with acetone and dried at 50 °C prior to their characterization.

In the PS technique nickel was loaded in the oil phase containing kerosene and 10% (v/v) D2EHPA by contacting equal volume of feed and oil phase at pH 4.6, resulting in quantitative loading of the nickel ions in the oil phase. The oil phase was separated and contacted with equal volume of oxalic acid solution for 30 min. The particles obtained were separated by centrifugation, washed and dried at 50 °C. In homogenous solutions the particles were synthesized by mixing aqueous solutions of nickel nitrate and oxalic acid retaining the same mole ratio (M) of nickel to oxalic acid as used in the ELM system. The total volume of the system was 100 ml.

Download English Version:

<https://daneshyari.com/en/article/151242>

Download Persian Version:

<https://daneshyari.com/article/151242>

[Daneshyari.com](https://daneshyari.com)