



Aqueous synthesis of high surface area metal oxides

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ABSTRACT

By applying high throughput synthesis and characterization technologies, we have been optimizing common dry or aqueous synthetic routes for the preparation of high surface area metals and oxides, such as precipitation and modified Pechini methods. For wet combustion synthesis, we have been screening a variety of organic acids as dispersants and developed proprietary recipes for individual metals. By resorting to easily decomposable organic acids (as opposed to citric acid in the original Pechini combustion method), such as glyoxylic acid, oxalacetic acid and ketoglutaric acid, it is possible to obtain high surface area materials for many metals after careful optimization of acid/metal ratio and calcination conditions. Examples are Sn, In, Co, Ru, Ni, Fe, Mn, Y, Ce and Rare Earth oxides and their mixtures. After calcination in the temperature range of about 300–400 °C, surface areas >150 m²/g could be obtained for Er, Tm, Co, Ru, and Nb; >200 m²/g for Sn, Fe, Mn, and Y; >300 m²/g for Ce; and >400 m²/g for Ni oxide. Noteworthy are also >140 m²/g for La₂O₃, >80 m²/g for CuO, and 75 m²/g for ZnO. For V, around 40 m²/g was possible for the nearly carbon-free V₂O₅, whereas up to 90 m²/g was obtained for a 90% V–10% carbon composite (by incomplete combustion of the organic acid). Residual carbon helps in stabilizing the porous oxide against sintering. Thus, conventional aqueous routes (precipitation, Pechini) can be competitive to more elaborate and costly methods such as those using organic solvents, sol–gel, supercritical drying or template/hydrothermal synthesis. Combustion synthesis is well suited for the preparation of mixed oxides from mixed metal solutions in aqueous organic acids. Bulk porous Co and CoRu mixed oxides have been screened for liquid phase alcohol oxidations and CoRuCe oxides for CO oxidation and VOC destruction, and doped NiO has been reduced to the metal and tested for various hydrogenations.

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1. Introduction

High surface area metal oxides are desirable absorbents, carriers and catalysts, and various synthetic methods starting from aqueous metal solutions or slurries have been applied. These include precipitation, hydrothermal synthesis, microemulsions as well as wet combustion synthesis. Auxiliary reagents such as acids or bases, templates, surfactants or dispersing agents are added to convert, immobilize or finely divide the metal precursors that upon subsequent drying and calcination are transformed to the corresponding oxides.

Organic solvent assisted routes such as solvothermal synthesis, sol–gel with or without supercritical drying, or oil drop methods are also widely used for the preparation of high surface area materials. The various traditional synthetic methods that are available for the

synthesis of inorganic nanoparticles have been extensively reviewed and evaluated [1,2]. Recently many more sophisticated methods for the preparation of nanoparticulated materials have been proposed, e.g. flame pyrolysis, arc and plasma discharge, sputtering, microwave irradiation, molten salt flux methods, solid state reactions, mechanical alloying, and inert gas condensation.

We have investigated the potential of three different traditional (dry or aqueous) routes, namely dry decomposition, precipitation and combustion synthesis from aqueous solutions, for the synthesis of high surface area metals and oxides starting from common and readily available metal precursors without making use of expensive templates, surfactants or alcoholic solvents or supercritical drying or high pressure equipment.

For liquid-phase combustion synthesis, we have been screening a variety of organic acids as dispersants and developed proprietary recipes for individual metals. Combustion synthesis is well suited for the preparation of mixed oxides from mixed metal solutions in aqueous organic acids. By resorting to easily decomposable organic acids (as opposed to citric acid in the original Pechini combustion

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method [1–5] or malic acid in a later modification [6]), such as glyoxylic acid and ketoglutaric acid, it was possible to obtain high surface area materials for many metals after careful optimization of acid/metal ratio and calcination conditions [7–18], for example, Sn, In oxides and their mixtures [8,9,12,14], yttria [15] and ceria [18]. Some catalytic applications of these high surface area metal oxides have already been published, for example, SnO₂ as carrier for emissions control [12], ceria as carrier for water–gas-shift catalysts [19], and Co–Ru mixed oxides for CO and total oxidations [20,21]. We have now applied and optimized combustion synthesis methods for additional metals such as Ni, Co, Fe, and Rare Earths and compared surface areas to those obtained by precipitation. We will summarize previous and recent results, classify metals according to most suitable acid dispersant and corresponding calcinations conditions and point out common trends.

2. Experimental

2.1. Equipment

2.1.1. Precipitation

Our integrated co-precipitation workflow has been published elsewhere [17,18]. Briefly, the workflow consists of an automated co-precipitation station, an automated particle recovery station, ovens for thermal treatment, and a parallel sample agglomeration and sizing system for particle sizing. The Symyx Software suite is used to design the, control the robotic actions and store the resulting data, and view the data. The co-precipitation station consists of a robot with eight parallel precipitation channels and 8 columns of 8 precipitation wells resulting in an 8 × 6 array of wells. Each channel has a pH probe, temperature probe, and three liquid addition probes that are robotically inserted into a disposable liner with magnetically coupled stirring. The Station is shown in Fig. 1. The precipitation can be carried out as a constant liquid addition, as a titration, or as a constant pH precipitation.

Precipitation or pH titration recipes were then scaled up in 250 ml three-neck flasks equipped with masterflex pH controllers and peristaltic pumps. Isolation of the precipitate was done by

centrifugation in two 40 ml vials followed by 4 wash steps in 40 ml vials. A typical temperature ramp was as follows: 55 °C/4 h ramp/120 °C/4 h hold/1 h ramp/350 °C/4 h hold in 40 ml vial.

2.1.2. Combustion synthesis

Libraries consisting of arrays of stirred tall 40 ml glass vials were loaded by powder or liquid dispensing robots with solid metal precursors and/or metal solutions as well as aqueous solutions of organic dispersants and/or solid organics, optionally aged at room temperature in open vials to evaporate part of the solvent (to induce gelation but also to prevent splashing and excessive foaming during the subsequent drying step), then dried and calcined in air in static calcination ovens. Amounts and process conditions used are detailed in the following tables.

2.2. Synthesis recipes

2.2.1. Dry decomposition

Common metal salts such as oxalate, acetate, carbonate, hydroxide were purchased from Aldrich, Alfa or Pfaltz&Bauer and used as supplied. Metal formates were prepared by slurring metal carbonate or hydroxide in excess formic acid followed by solvent evaporation. The dry powders were calcined in air in tall 40 ml vials according to the following representative heat up protocol: 55 °C/1 h ramp/120 °C/1 h hold/1 h ramp/325 °C/4 h hold.

2.2.2. Wet combustion synthesis

A general recipe consists of dissolving or slurring the metal precursor (acetate, nitrate, hydroxide) in aqueous organic acid (glyoxylic acid OHC-COOH, ketoglutaric acid or acetone-1,3-dicarboxylic acid HOOC-CH₂-CO-CH₂-COOH, oxalacetic acid HOOC-CH₂-CO-COOH) in a tall 40 ml glass vial followed by calcination in air. A typical heat up protocol is as follows: 55 °C/4 h ramp/120 °C/4 h hold/1 h ramp/300 °C/4 h hold.

2.2.3. Synthesis of Ni–Ce–Pd by the modified Pechini method

1 g Ni hydroxide was dissolved in 6.5 ml 20% aq. glyoxylic acid in a 40 ml glass vial, then appropriate amounts of solid Ce acetate and ammonium Pd oxalate were added under stirring to obtain a

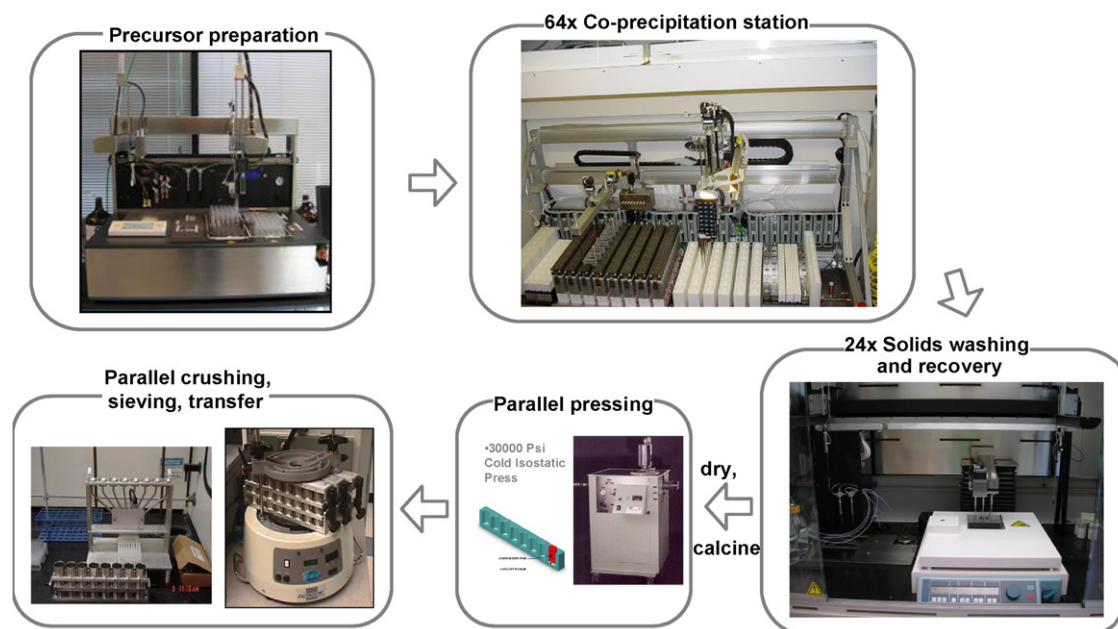


Fig. 1. Co-precipitation station and supporting catalyst synthesis hardware.

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