



Solution combustion synthesis of nano-catalysts with a hierarchical structure



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ABSTRACT

The structure, composition, surface area and catalytic activity of Solution Combustion Synthesis (SCS) catalysts are all influenced by the conditions of preparation and in particular, the glycine concentration in the initial SCS solution. NMR was used to monitor the formation of glycine-nickel nitrate complexes in solution before SCS initiates, IR high speed temperature measurements have allowed to elucidate the mechanism of synthesis during SCS, dynamic X-ray analysis and thermogravimetric analysis have clarified the mechanisms of phase formation during SCS, BET analyses have shown the regularity of pore formation and SEM and TEM studies have indicated the regularities involved during microstructure formation. Regular three-dimensional (3D) flowerlike Ni-NiO hierarchical architectures were synthesized by SCS. The results have revealed a three-dimensional percolation network with hierarchical structure on the basis of nano-structured metal oxides and metals synthesized during SCS. Such hierarchically nanoporous catalysts have versatile structural properties such as increased surface area and large overall pore volume that can alleviate diffusional limitations of conventional nanocatalysts with solely microporous framework. This is important for liquid phase heterogeneous catalysis. These new insights provide a valuable capability for optimizing the selectivity and activity of SCS catalysis and will no doubt be of significant interest to a wide range of researchers working in catalysis and other fields.

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1. Introduction

A combination of SHS and reactive solution approaches leads to the so-called solution (or aqueous) combustion synthesis (SCS) method [1]. This process typically involves a reaction in solution of metal nitrates and different fuels.

SCS entails significant advantages over other combustion-based methods and the most critical are mentioned below:

- (1) The initial reactants mixing takes place in the liquid state, facilitating control over homogeneity and stoichiometry of the reaction products.
- (2) The possibility of impurity ions incorporation in the oxide hosts is a viable option, in order to prepare materials of industrial interest (pigments, phosphors, catalysts, etc.).

- (3) The process is fast and requires no special equipment, which makes it preferable over SHS methods.
- (4) The method is very rapid allowing the formation of metastable phases [2].

Solution Combustion Synthesis (SCS) is a simple, but important technique for the synthesis and processing of nano-structured metals, oxides, spinels, alloys, intermetallics etc. SCS is based on exothermic redox reactions between nitrates (oxidizers) and organic substances (reducers) to directly produce nano-structured powders [3,4]. More specifically, after preheating to moderate temperatures (approximately 150–200 °C), the reaction can be initiated and the combustion front propagates a rapid (typically 0.001–0.1 m s⁻¹) high-temperature (1000–3000 °C) wave in a self-sustained manner through the system, leaving behind fine solid product of tailored composition [1].

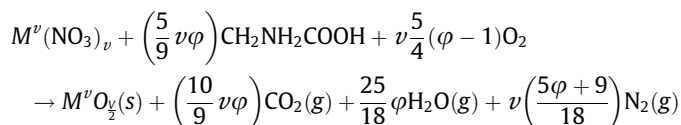
The mechanism ruling the SCS process and the key role played by the reducing agent is crucial, as well. It is interesting to mention that various fuels have been employed for specific classes of oxidic

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materials. Various water soluble organic substances are utilized as source of carbon and hydrogen that, on combustion, form carbon dioxide and water generating heat during the reaction [5,6]. Furthermore, certain fuels, such as glycine, act as complex formation agents with the metal cations, which enable high mixing homogeneity in solution and hence avoid segregations [7,8]. Such compounds that contain N–N bonds are well-known to better assist the combustion reaction; however, there is the drawback of releasing NO_x emissions during combustion. In some cases, the use of highly viscous fuels, such as glycerol, facilitates better distribution of the final desired product on the structured catalyst support [9].

The reaction between a metal nitrate as an oxidizer and glycine (C₂H₅NO₂) as a fuel is typically presented as follows:



where ν is the metal valence and a tunable parameter, φ is the fuel-to-oxidizer ratio. In case of $\varphi = 1$, all oxygen required for complete combustion of fuel is derived from the oxidizer, while $\varphi > 1$ signifies fuel-rich (or lean) conditions [10].

According to the equation above, the solid products of SCS should be oxides, and thousands of different oxide-based nanopowders are indeed synthesized by this technique. However, an appropriate fuel/oxidizer ratio in fuel rich conditions results in the formation of metallic phases, instead or co-existing with oxides [7]. Kumar et al. investigated the reaction pathways of metal nanopowders using nickel and copper as examples [11,12]. They reported, concerning the nickel-glycine system, that nickel oxide was formed at the early stage in the reaction front, and it was subsequently reduced to nickel in the post combustion zone.

It is well-known in the field of catalysis, that nano-sized catalysts exhibit impressively high activity and selectivity [13]. Nano-composites containing metals and metal oxides can also be obtained by SCS and offer a strong promise for increasing both the catalytic selectivity and the activity of nano-catalysts [14,15].

The activity of catalysts of different structures and compositions was studied during hydrogenation in the liquid phase, since this process is extremely sensitive to the slightest structural changes in the catalyst [16]. Heterogeneous catalytic hydrogenation uses finely crushed metal catalysts such as platinum, palladium, ruthenium, rhodium, osmium, copper and nickel either in pure form as pellets or coated on inert carriers [17–24] which are insoluble in organic solvents. The most active among them are ruthenium and rhodium, but platinum and nickel are the most widespread, the latter mainly because it is much cheaper. Hydrogenation of alkenes with a catalyst is usually carried out at ambient pressure and at a temperature of 20–80 °C in alcohol, acetic acid or water.

SCS produces nano-powders in a single step by a simple and rapid process [3,4]. Their specific surface area is usually small (up to 10 m²/g), while in some cases it can be extremely high. For example, Cross et al. [15] report Ni nanoparticles with extremely high surface area (155 m²/g) supported on fumed silica (SiO₂) as catalysts for the ethanol decomposition toward hydrogen at low temperatures (200 °C). In order to prevent the undesired oxidation process that follows the formation of the highly dispersed nickel nanoparticles, the synthesis was conducted in an inert atmosphere. Interestingly, the low oxygen concentration during combustion passivated the nickel nanoparticles through the formation of a thin amorphous oxide layer.

In the present study, hydrogenation was carried out in the liquid phase at 80 °C on Ni/NiO SCS derived nano-catalysts. It was found that their physical properties and structure depend in a

complex way on the parameters of SCS processing, composition of the initial SCS solution [25] and even the amount of water used in the initial solution [26]. Various reaction mechanisms (mainly at the atomic-level) have been identified as being active during the synthesis of these materials which critically influence their catalytic properties. Controlled hydrogen adsorption studies have helped to clarify the main mechanisms involved. Understanding the interrelationships between the processing parameters and the ensuing structure has allowed a degree of optimization of the catalytic properties of the new catalysts.

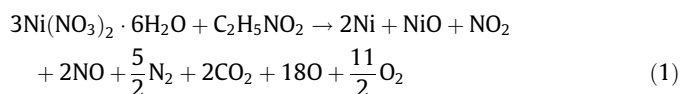
2. Methodology

2.1. Materials

| Material | Manufacturer | Assay |
|---|----------------|-------------|
| Nickel (II) nitrate hexahydrate for analysis [Ni(NO ₃) ₂ ·6H ₂ O] | Merck | 99.0–102.0% |
| Glycine for synthesis [CH ₂ NH ₂ COOH] | PanReac | 99.0% |
| Maleic acid [HOOCCH = CHCOOH] | AppliChem | |
| | Riedel-de Haën | 99.0% |

2.1.1. Solution combustion synthesis of Ni-based catalysts

The initial solution contains nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) as the oxidizer with glycine as the reducer. In the series of experiments carried out, four types of samples were synthesized keeping the quantity of nickel nitrate constant at 9.34 g in the initial mixture with 75 ml distilled water, adding specific amounts of glycine (80, 60, 50 and 40 wt% of nickel nitrate) to achieve fuel to oxidizer molar ratio (φ) of 2.78, 2.08, 1.74 and 1.4 for the production of Ni and NiO where $\varphi = 1.0$ corresponds to the stoichiometric composition for the equation (1), below.



Each solution was pre-heated in a borosilicate glass beaker on a hot plate with mild magnetic stirring until the temperature reached 70 °C and then placed in a pre-heated furnace at 500 °C to initiate SCS, yielding an extremely friable foam-like structure consisting of nano-sized powders lightly bound together. Once SCS is completed the beaker is removed from the furnace and allowed to cool at room temperature.

2.2. In-situ monitoring and characterisation of the SCS process

Determination of the temperature and velocity of the combustion wave during SCS was carried out using three 100 μm diameter K-type (chromel–alumel) thermocouples placed in and above the solution. A PICO TC-08 conditioner was used to convert, filter and amplify the temperature signals which are recorded at a rate of 0.5 ms. No attempt was made to move the thermocouples since these measurements were used only to pinpoint the reaction time and correlate it to the appearance of combustion phenomena. In any case, this work is being extended in order to compare the measured reaction temperatures with calculated adiabatic reaction temperatures and will be published later. The temperature of the combustion wave was also measured in-situ using a high-speed infrared camera (FLIR Systems, model A655SC). The speed of the combustion wave was calculated by analysis of the data obtained from the high-speed infrared camera.

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