Influence of atomic structure on the nano-nickel-based catalyst activity produced by solution combustion synthesis in the hydrogenation of maleic acid

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ABSTRACT

Nanostructured nickel-based catalysts have been produced by solution combustion synthesis (SCS) and it has been found that their physical properties and atomic structure depend in a complex way on the parameters of SCS processing, especially the amount of water used in the initial solution. The catalysts were characterized by XRD, BET, and GC-IRF and their catalytic activity for hydrogenation of maleic acid was determined. Various mechanisms (especially at the atomic level) are active during these materials syntheses that critically influence their catalytic properties, often in opposing ways. Hydrogen adsorption studies have helped to clarify the main mechanisms involved. Specifically, it was determined that nickel oxide acts as a carrier for nanostructured metallic nickel, in the absence of which the catalyst almost deactivates. Understanding the interrelationships between the processing parameters and the ensuing atomic structure has allowed a degree of optimization of the catalytic properties of the new catalysts.

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1. Introduction

Solution combustion synthesis (SCS) is a recent development in catalyst synthesis compared with traditional methods and other solid state combustion synthesis routes [1]. SCS is based on self-sustaining redox reactions in a homogeneous aqueous solution of reactants (oxidizers and fuel), which, when rapidly heated in a furnace, lead to the formation of solid, mostly crystalline, nanostructured powder [2]. In a preheating temperature range of 300–600 °C the water is rapidly vaporized; the remaining reactant solution dries and heats up and within at most a few minutes it ignites and sustains a rapid exothermic reaction, resulting in foamlike nanostructured powder forms with an apparent density many times lower than that of the original solution. The actual reaction temperature during the exothermic synthesis reactions varies between 700 and 1500 °C, depending on the actual system. Depending on the fuel used and its proportion in the initial solution, the combustion type can be distinguished as nonflaming, flaming, or explosive. Depending upon the conditions and the reactants used, the reaction occurs as a through-the-volume reaction or layer by layer [2].

There are three main features that distinguish SCS from other combustion routes. First, all the ingredients are mixed in an aqueous solution at a molecular level. Second, the reaction that is responsible for the SCS final solid product can be different from that responsible for the self-sustained combustion. The oxidation of organic fuel evolves the majority of heat, while the SCS products are mainly nanostructured metals or oxides. Third, the SCS processes have a large amount of gaseous byproducts, such as N_2, CO_2, and H_2O. Such gasification leads to a significant expansion of the final product (into a nanostructured foam in many cases) and rapid cooling after the reaction, which makes the solid products porous and very finely dispersed [3].

There are two main modes of SCS that can be utilized for synthesis. The first mode is called the self-propagating combustion mode, in which a small amount of the initial solution is heated locally in order to initiate the exothermic reaction, which then self-propagates through the rest of the volume in a combustion wave form. The second mode is called volume combustion or thermal explosion. In this mode, the reactive solution is heated uniformly to the boiling point of the solvent (Stage 1). The next preheating stage contains a relatively long constant-temperature

range where the free water and a portion of the bound water evaporate (Stage 2). This stage is followed by a higher evaporation rate, and at some temperature (ignition temperature), the reactions initiate and the solution suddenly increases to the maximum temperature (Stage 3), forming the nanoproduct. Finally, the product goes through a cooling process, the final stage of SCS (Stage 4) [4,5].

As a nanostructured materials synthesis method, SCS offers many advantages over other methods, including relatively low preheating temperatures and rapid completion rates, while the equipment needed is simple and the reactants used are generally very inexpensive; for example, the fuel used is generally either urea or glycine [6]. Recently, a number of specialized SCS approaches have also been reported, such as a volume combustion mode, self-propagating sol–gel combustion, impregnated inert support combustion, and impregnated active support combustion [5,7]. A disadvantage of the SCS method is the emission of NO_x during the reaction, originating from the fuel used and its reaction with metallic oxides during the exothermic reactions [3]. Naturally, such emissions are generally trapped using scrubbers.

Kumar and co-authors [4] concluded that glycine's decomposition starts at approximately 242 °C and that the main product of that decomposition stage is NH_3, while CO and HNCO are formed in the temperature range 312–457 °C [8]. When SCS is used for the synthesis of Ni-based materials, the decomposition of nickel nitrate hexahydrate includes several stages as well [9]. During the first stage, at 37–77 °C, the water evaporates. The second stage (147–187 °C) involves the partial decomposition of the nitrate, which forms $Ni(NO_3)(OH)_{0.25}\cdot H_2O$, which decomposes during the third stage (257–297 °C), producing Ni_2O_3, HNO_3, and H_2O. Further analysis of these results indicates that both decomposition and combustion reactions occur in the same temperature range of 237–347 °C. It was also noted that the oxidizer and fuel simultaneously supply the gaseous products HNO_3 and NH_3, which are a highly exothermic mixture [10]. They also reported the equilibrium products and the adiabatic temperatures of the $HNO_3 + NH_3 + NiO + H_2O$ system. Their results revealed that this system is characterized by a reasonably high adiabatic temperature (427–627 °C) and there are three distinct regions of products depending on the concentration of NH_3. At low NH_3 amounts, NiO remains unreduced, while increase of NH_3 content results in the formation of NiO–Ni or Ni phases. As hydrogen concentration increases with the increase of NH_3, this leads to the conclusion that increasing the amount of glycine in the initial solution leads to the formation of reductive gases such as NH_3 and H_2 in the first stage of combustion. Such variation of the gaseous species composition results in a change in the production of solid products from NiO to NiO–Ni mixture to pure Ni.

The main driving force of the combustion process in the nickel nitrate–glycine system is the highly exothermic reaction between the gases N_2O and NH_3. N_2O forms during the decomposition of nickel nitrate hex hydrate at 250 °C, while NH_3 is yielded as one of the main products of glycine's decomposition. It was thus concluded that the combustion reaction is triggered by an exothermic reaction between N_2O and NH_3. However, there are two endothermic steps that are responsible for the formation of the metallic phase in the SCS solid products. In the first step, the decomposition of nickel nitrate at ~250 °C forms NiO nanoparticles. The second step takes place at higher temperatures (above 450 °C), in which the reduction of NiO occurs by excess of NH_3 to metallic nickel [3].

In most SCS cases nitrates are used to produce oxidizers—the NO_3^- ions—that have high solubility in water and that facilitate starting solutions with high concentrations. As mentioned, urea and glycine are the most common fuels utilized in SCS, as they are relatively cheap and have high exothermicity. Although hydrazine-based fuels have also been reported [2,11], they are rarely used because of their inherent toxicity. Other organic fuel options reported are alanine, asparagine, serine, methyl cellulose, ammonium acetate, ammonium citrate, ammonium tartrate, and combinations of fuels, such as citric acid and glycine [2]. All these fuels are sources of carbon and hydrogen during the reaction, which form complexes with metal ions, facilitating the solution's cations' homogeneous mixing [3]. Some of the fuels have been reported to be specific for particular catalytic processes [12].

The role of the reducer (fuel) in the SCS process is not only to provide sufficient heat for combustion to take place, but also to help form stable complexes with the metal ions to increase their solubility and prevent selective precipitation of metal ions during water evaporation and removal [13,14].

Organic substances that can be employed in SCS as a reducer should have the following properties [15]:

- They should be soluble in water. Additional organic fuel can be used to improve fuel solubility.
- The ignition temperature should be below 500 °C and the melting point below 250 °C.
- The organic fuel is usually decomposed during the reaction, producing large amounts of gases that improve catalysts' nanotextural properties.
- They should act as metal dispersing and/or complexing agents that would lead to the formation of new metal–fuel precursors.

For the above reasons, glycine is very popular as a reducer for preparing a variety of mixed metal oxides by SCS. The final nanostructured powder properties depend strongly upon the reaction between the fuel and the oxidizer [16].

Because of the capability of direct synthesis of nanostructured powders, SCS has been used to produce a wide variety of technologically useful oxides with dielectric [17–21], magnetic [2], mechanical [2], electrical [22], luminescent [23,24,27,28,30], optical [25–27,29,30], and catalytic [31–40] properties. Highly active catalytic materials prepared by SCS include Al_2O_3 and MAl_2O_4 (M = Mn and Zn) spinels, which are also used as catalysts' supports [31,32]. Many metal–spinel composites (M = Fe–Co/Ni) and M/Al_2O_3 (M = Pt, Pd, Ag, and Au) composites are SCS catalytic systems. Especially M/Al_2O_3 composites often exhibit better catalytic properties for oxidation of carbon monoxide and hydrocarbon and reduction of NO_x than the traditional Pd or Pt catalysts [33–40]. These enhanced catalytic properties are probably due to the ionic substitution that occurs during SCS, which is generally not feasible with other chemical processes, including sol–gel [2].

Catalytic hydrogenation is used in the large-scale production of many chemicals [41–43], a very important example being ammonia, which is prepared via the Haber process of hydrogenation of nitrogen [44]. In food processing, one of the best-known applications of catalysis is the hydrogenation of fats using nickel catalysts to produce margarine [45]. Nanosized metal catalysts have catalytic properties (activity, selectivity, and stability) during hydrogenation superior to those of Ni Raney catalysts [46], and many nickel-based nanosized catalysts have been reported for many hydrogenation processes [44,47–50], apparently because nickel surfaces readily adsorb hydrogen [46]. Nickel activates hydrogen very easily in the atomic state, and this is essential for hydrogenation of unsaturated hydrocarbons. Due to their low price, easy availability, and high reactivity in this class of reactions, such catalysts have received increasing industrial attention in recent years.

There are a number of recent reports of preparation of catalysts for various processes by SCS. A series of active nanosized Ni–Al_2O_3 catalysts for the catalytic methanation of CO were prepared by SCS of Ni^{2+} and Al^{3+} nitrates with urea [51]. The main influence of the combustion process on the physicochemical and catalytic properties of those Ni–Al_2O_3 catalysts was investigated by changing the reducer/oxidizer ratio. Furthermore, nanostructured MnO_x cata-