

Solution Combustion Synthesis of Nano Materials

P. Dinka* and A. Mukasyan**

Department of Chemical and Biomolecular Engineering

University of Notre Dame,

Notre Dame, IN 46530, USA

* pdinka@nd.edu; ** amoukasi@nd.edu

ABSTRACT

The results on novel approaches for synthesis of nano-sized materials by utilizing a Solution Combustion (SC) method are presented. Four different reaction modes were investigated, including Volume (VC), Sol-Gel (SGC), Impregnated Paper (IPC) and Impregnated Support (ISC) Combustions. By using these approaches complex $\text{La}_{0.6}\text{Ce}_{0.4}\text{Fe}_{0.68}\text{Ni}_{0.2}\text{K}_{0.12}\text{O}_3$ perovskite-based catalysts were synthesized. Obtained products were characterized by their microstructures and specific surface areas (SA). The range of the SA for as-synthesized samples was 20-50m²/g with the following order for the SA values: IPC~VC<SGC<ISC. The catalysts activities were tested for auto thermal reforming of the high hydrocarbon fuel (JP-8 surrogate with 10 ppm of sulfur) for hydrogen production. All synthesized catalyst showed a high fuel conversion and stable performance. It was also revealed that catalysts activity has no direct correlation with their SA but it mostly depends on the powder sinterability.

Keywords: nano-powders, combustion synthesis, auto thermal reforming, hydrogen

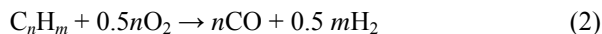
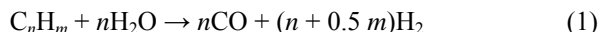
1 INTRODUCTION

Fuel cell energy systems have attracted much attention due to their high efficiency and zero- emission. Proton exchange membrane fuel cell (PEMFC) is one of the most promising technologies for fuel cell utilization. The ideal fuel for PEMFC is **pure hydrogen**, which is not available as a fuel in nature and it needs to be produced from other sources. The technical limitations associated with difficulties of hydrogen transportation, storage, and handling require the use of hydrogen rich gas obtained from liquid organic fuels.

It is a special task to convert **JP-8 fuel**, as it is widely used for most military vehicles, with developed logistical system. However, it is a great challenge to reform such a fuel, because JP-8 involves high hydrocarbon, as well as aromatic compounds. Moreover it also contains a significant amount (800 ppm) of sulfur. It is well recognized that during reforming, the fuel with such composition has a vast tendency to a **carbon formation on**

catalyst, which leads to catalyst rapid poisoning and reaction termination [1, 2].

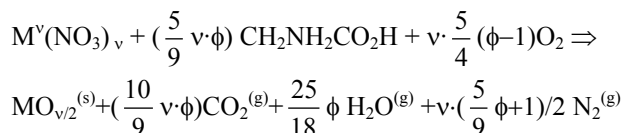
The conversion of hydrocarbon fuels to H₂ can be carried out by several catalytic reaction processes, including steam reforming (SR) (reaction 1), partial oxidation (PO) (reaction 2) and autothermal reforming (ATR), which **combines** SR and PO reactions. The former has high hydrogen yield, but is endothermic. The latter (PO) is highly exothermic, but yields less hydrogen. Thus ATR process provides higher efficiency and energy density than other conventional processes [3]. Also, a presence of oxygen decreases coke deposition on catalyst [4]. Note that two additional reactions take place during ATR; i.e. water-shift reaction (3), which increases hydrogen yield and undesired hydrogen consuming methanation (reaction 4):



The catalysts for a steam reforming of sulfur containing, higher hydrocarbons typically comprise expensive noble metals, such as Pt, Rh, and Ru [5]. Complex mixed metal oxides with **perovskite** structure attract significant interest in many areas of solid state chemistry including catalysis [6]. The general formula of perovskites is ABO_3 , where A is a metal with larger ionic radii, typically from rare-earth group and B is a metal with smaller radii, usually from transition metals group. Partial substitution of A, B or both sites allows one to synthesize a wide variety of compositions with different properties.

Different techniques are used for perovskite preparations, including sol-gel [7], solid-state method [8] mechano-synthesis [9] and **combustion synthesis** [cf. 10]. The latter is an attractive method for production of advanced solid-state materials. The specific feature of this technique is that after its local ignition, a self-sustain propagation of the reaction front occurs throughout the heterogeneous powder mixture of reactants, living behind the desired products. Modification of this technique, so-called **solution combustion** (SC) synthesis, occurs in a liquid mixture of metals nitrites (oxidizer) and a fuel such

as glycine, citric acid or urea. At elevated temperature (120-170 °C) the reaction self-ignites through the entire volume (so-called Volume Combustion mode) leading to the formation of fine solid products with tailored composition. The combustion reaction can be described by following general scheme (5):



v is a metal valency, ϕ is a fuel to oxidizer ratio, e.g. $\phi=1$ means that the initial mixture does not require atmospheric oxygen for complete oxidation of a fuel, while $\phi>1$ (<1) implies fuel-rich (lean) conditions.

The **specific features** of solution combustion synthesis contribute to the unique properties of the synthesized products. First, the reaction media being initially in the liquid state (e.g. aqueous solution) allows mixing the reactants on the molecular level, thus permitting precise and uniform formulation of the desired composition on the **nano scale**. Second, the high reaction temperature ensures high product purity and crystallinity in one preparation step. Third, short process duration and the formation of various gases inhibit particle size growth and favor synthesis of **nano-size powders** with high specific surface area.

In our previous work we have demonstrated that partially substituted perovskite-based catalyst from LaFeO₃ family are active and have a good resistant to coke deposition during ATR of JP-8 surrogate fuel, which does not contain sulfur [11]. Further we showed that modified perovskite-based catalyst prepared by SC technique shows **stable performance** during reforming of JP-8 fuel contains up to **50 ppm of sulfur** [12].

Recently, we developed novel modifications of the solution combustion synthesis [13]. In this work we present results on comparison of properties of **nano-sized materials** synthesized by these **combustion approaches**.

2 EXPERIMENTAL

2.1 Catalyst preparation methods

As mentioned above, several modifications of the solution combustion synthesis were used to produce high surface area catalysts. These approaches can be briefly described as follows:

1. **Volume Combustion Mode (VC)**: this conventional process involves reaction of desired amount of metals nitrates (oxidizer) with glycine (fuel) dissolved in water and heated on hot plate. After water evaporation, the temperature of the mixture rapidly increases, achieving ignition point (~130°C) when reaction spontaneously initiates, leading to formation of product with desired composition. The maximum

reaction temperature is ~1000°C and process duration of ~10 seconds.

2. Self-propagating **Sol-Gel Combustion (SGC)**: the desired amount of metals nitrates + fuel solution is dried to make a sol-gel like heterogeneous media, which was preheated to 30-80°C, followed by local reaction initiation by a heated tungsten wire (igniter). As a result a self-sustain reaction wave steadily propagates along the media forming nano-powder of desired composition. Characteristic velocity of the combustion front propagation is ~ 1 cm/s with maximum temperature ~500°C and process duration ~1 second.
3. **Impregnated Paper Combustion (IPC)** method: solution of metals nitrates with glycine is impregnated to thin pure cellulose paper and dried at room temperature. After drying, such prepared media is locally ignited at room temperature and steady combustion front propagates along the impregnated paper. In this case, the maximum reaction temperature can be as high as 1000°C but reaction time, owing the rapid quenching of thin reacted thin layer, is less than 1 second.
4. **Impregnated Support Combustion (ISC)** approach, which involves dipping of porous inert supports into a desired reactive solution, followed by reaction initiation similar to those in VC or SG modes (see ref. [14] for details).

Using these four approaches La_{0.6}Ce_{0.4}Fe_{0.68}Ni_{0.2}K_{0.12}O₃ composition, which was shown to be optimum for the JP-8 fuel reforming [12], was synthesized. The corresponding metal nitrates (Alfa Aesar) and glycine were used as the precursors for perovskites synthesis by using reaction (5). Obtained products were characterized by BET, SEM, EDS, XRD and chemical analysis to verify products microstructure, as well as phase and chemical compositions.

2.2 Activity test

Testing of catalysts in autothermal steam reforming of JP-8 surrogate was performed in continuous flow system with fixed bed tubular quartz reactor (7mm ID) at atmospheric pressure. The catalysts were reduced prior the reaction at flow of 5 % of hydrogen in nitrogen at 800 °C. The flow was maintaining at this temperature for 2 hours and then the reaction was initiated by reactant introduction. The experiments were performed under following conditions: H₂O/C = 3, O₂/C = 0.35, temperature: 800 °C, gas hourly space velocity (GHSV) = 130000 h⁻¹. The reactor effluent was cooled in a condenser, thus separating water and unreacted hydrocarbons from the gas stream. Gas stream were analyzed by means of gas chromatograph Agilent Micro GC 3000A, equipped with thermal conductivity detector, using a molecular sieve and Plot Q column with argon and helium as a carrier gases respectively.

The reaction activity tests were conducted with a surrogate of JP-8 fuel [15]. This representative blend, in molar percent contains 34.7% n-dodecane, 32.6% n-decane, 16.7% methylcyclohexane and 16.0% tert-butyl benzene. Using a model fuel with defined composition enabled thermodynamic calculations and thus proper evaluation of experimental results. 1,4-thioxane was added to the JP-8 surrogate as the sulfur compound in such amount to contain 10 ppm of sulfur.

Catalytic activity was evaluated in terms of hydrogen yield, which is defined by formula:

$$Yield(\%) = \frac{n(H_2)}{n(H_2O) + b \times n(C_aH_b) / 2} \times 100$$

where $n(H_2)$ is a molar concentration of hydrogen in product and denominator represents an overall amount of hydrogen in the system in the form of fuel $n(C_aH_b)$ and stoichiometric amount of water.

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

Typical data of XRD analysis for as-synthesized (e.g. VC mode) product is shown in Figure 1a. It can be seen that the material contains as a major phase $La_xCe_{1-x}Fe_{0.68}Ni_{0.2}K_{0.12}O_3$ perovskite. However, the Ce_7O_{12} phase is also present suggesting that not all Ce was incorporated to a desired lattice. Similar phase compositions were observed for perovskite prepared by SG and IP method. Note that the crystallinity of as synthesized materials increased in the following order: SGC < IPC < VC.

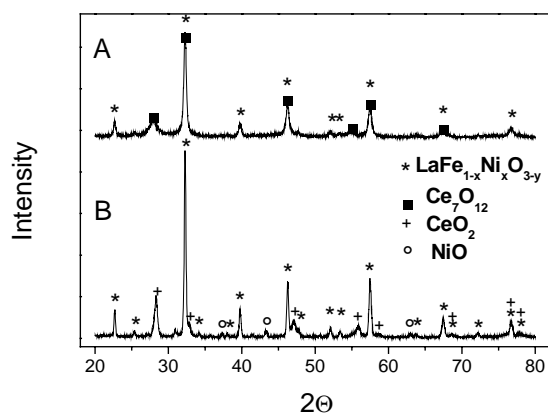


Figure 1. XRD patterns of $La_{0.6}Ce_{0.4}Fe_{0.68}Ni_{0.2}K_{0.12}O_3$ perovskites prepared by VC method before (A) and after (B) activity test.

After the catalytic activity test, the crystallinity of phases improved (Fig.1b) and Ce_7O_{12} phase was transformed to CeO_2 . It is more important that a new phase, i.e. NiO was also detected. The latter is a result of catalyst treatment in strong reduction atmosphere which

leads to the formation of isolated nickel nucleus on the perovskite surface [16]. Note that after high temperature treatment Ni particles, as exposed to air, were reoxidized.

Figure 2 presents the typical surface morphologies of the catalysts synthesized by different combustion methods. Distinct differences in microstructures of the materials prepared by these approaches can be observed.

The ISC-catalyst has a spongy-like extremely porous micro structure (Fig.2a). In turn, SGC method forms spherical aggregates with the size of about 0.5 – 5 μm (Fig.2b). Material synthesized by VC shows very low porosity with presence of some irregular aggregates of various sizes (Fig.2c). Finally IPC product (Fig.2d) has similar morphology with VC but it is more porous.

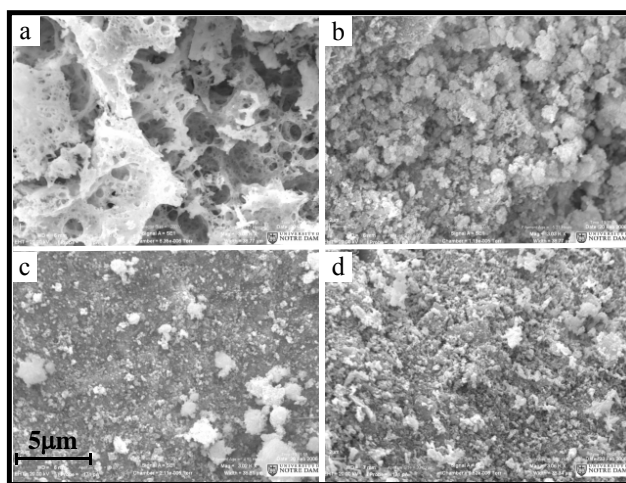


Figure 2. SEM image of $La_{0.6}Ce_{0.4}Fe_{0.68}Ni_{0.2}K_{0.12}O_3$ perovskite prepared by different solution combustion approaches: (a) ISC using Al_2O_3 activated support; (b) SGC; (c) VC; (d) IPC.

The results on BET measurements (see Table 1) support these microstructural observations, giving the following order for values of specific surface areas for samples synthesized by the methods: IPC~VC < SGC<ISC.

Table 1. Specific surface area and reaction activity of catalysts prepared by different method.

Method of synthesis	S synthesized [m ² /g]	S after reaction [m ² /g]	H ₂ yield [%]
VC	21.3	4.4	36.7
SGC	27.9	4.9	30.7
IPC	21.6	5.3	39.3
ISC, Al_2O_3	48.8	38.3	20.7

3.2 Catalyst activity test

The typical products composition and fuel conversion, using catalyst prepared by VC are shown in Figure 3. It can be seen that ~ 83 % conversion was maintained during the whole duration of the experiments (12 hours) with hydrogen concentration ~35 %. The hydrogen yields calculated based on such measurements of products compositions for different catalyst are shown in Table 1.

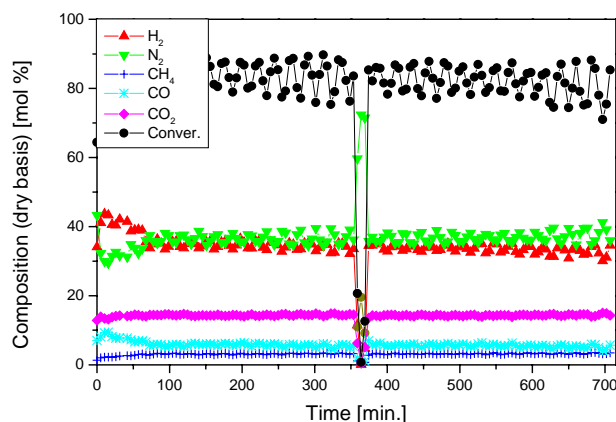


Figure 3. Product gas composition and reaction conversion obtained during steam reforming of JP-8 surrogate on catalyst prepared by VC method.

It can be seen that the highest activity in autothermal steam reforming of JP-8 surrogate, containing 10 ppm of sulfur at temperature of 800 °C was achieved on catalyst synthesized by IPC method. This result does not correlate with the specific surface areas of the as-synthesized catalysts. The observed effect can be attributed to the different sinter abilities of the powders. Indeed it was shown (Table 1) that among unsupported catalysts (i.e. SGC, VC, IPC) the IPC powder possessed the highest surface area after the test. The lower performance of the high surface area supported catalyst (ICS) can be explained by not optimized chemical composition of the support (Al_2O_3) [17, 18].

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