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## Nanostructural evolution in mesoporous networks using in situ High-Speed Temperature Scanner

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### ABSTRACT

Mesoporous networks with a special distribution of functional centers are an important class of high performance materials for catalysts, bioscaffolds, energy conversion and storage systems. Methods of fabrication allowing to control over special distribution of the functional sites of required phases and designed morphology are still of a great challenge. Here, we report a wet-combustion method for functionalization of the mesoporous network of alumina nanofibers with a single fiber diameter of  $7 \pm 2$  nm by Ni-based nanoparticles. The second-scale duration of the combustion process developing high flame temperature ( $> 1000$  °C) allows fabrication of mesoporous functional networks with tailored size, morphology and homogeneity of the dopants in a single-stage. The mechanism of the combustion process are studied by in situ high-speed temperature scanner, which continuously records the temperature history and applied power during the process. It readily allows quenching of the samples at a specified point, demonstrates the critical effect of a fuel on the decomposition temperature, combustion enthalpy, functional group, and pH. As a result of the wet-combustion synthesis, aligned double core-shell NiO-NiAl<sub>2</sub>O<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> fibers or NiO nanoparticles deposited onto alumina nanofibers can be formed.

### 1. Introduction

Mesoporous ceramics are widely used elsewhere, including but not limited to catalysis, energy and biomedicine, owing to their high surface area, narrow pore size distribution, high lifetime expectancy and stability [1–4]. The high surface area allows a large number of active sites for extensive adsorption of a wide variety of different species and initiation of surface or interface related processes [5]. In general, mesoporous ceramic materials are expected to exhibit fast kinetics for gas release and subsequent uptake of gas [6]. These features make the mesoporous materials excellent candidates for gas and energy storage, catalyst and catalyst support, membranes and filters. In addition, mesoporous networks are reported to exhibit extraordinary mechanical, electrical, biomedical and optical effects, due to nano-confinement effects in nanochannels and shortening the transport path of electrons and ions [5,7,8].

Often the mesoporous host should be designed and functionalized to

exhibit enhanced properties for specific target applications including catalysts. For instance, the mesoporous networks doped by transition metal oxides possess high performance in a wide range of catalytic reactions [9]. The activity and stability of catalysts are dictated by the morphology, composition and distribution of the functional dopants. Therefore, the functionalization of the mesoporous materials with dopant of designed architecture is critical for the development of materials with tailored catalytic properties.

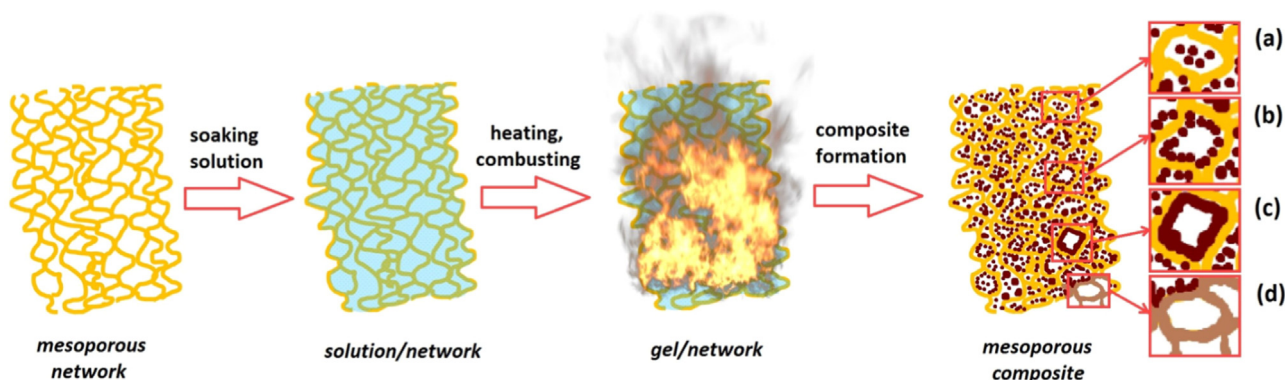
Recently, one-stage wet-combustion method was successfully applied for deposition of copper oxide nanoparticles on a mesoporous network of alumina [10]. The wet-combustion method is based on combination of dip coating and solution combustion techniques providing deposition of different materials on a mesoporous network with a tunable microstructure and possibility to manipulate by the interaction between a host and a functional material. The high-flame temperature, generated during the combustion process, lasts few seconds leading to the formation of nanoscale particles in a single-stage without

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**Fig. 1.** Schematic representation of wet-combustion synthesis: The wet-combustion method includes soaking mesoporous framework in the reactive solution heated at elevated temperature. As a result mesoporous materials with different structure: (a) Nanoparticles in the mesoporous network; (b) Nanoparticles attached to the mesoporous network; (c) The mesoporous network covered with a continuous layer; (d) Hybrid mesoporous network forms.

a need for calcination. The wet-combustion method involves infiltration of a reactive combustible solution into the mesoporous network due to the capillary forces, and a subsequent heat-treatment for ignition of a self-sustaining combustion process (Fig. 1).

Crucial influence of the nature of fuel on the pathway of the reaction, chemical composition and morphology of the end-product is a well-established fact [10–13]. The combustion behavior of metal nitrate – fuel system is highly dependent on a fuel type [10,13,18]. For instance, the effect of the on the composition and the final morphology of product as well as the mechanism of reaction can be drastically different, using glycine, urea and citric acid differentiating at functional groups, enthalpies of combustion, decomposition temperature and mechanism (Fig. 2).

Depending on the coverage of the decomposition temperatures of the metal nitrate-fuel system, the mechanism of the combustion process can be cardinally changed. Moreover, the heat generated during the combustion of the fuels differs significantly (Table 1).

To prepare the composition of designed morphology, it is important to set the compatible metal precursor-fuel pair and ratio. Therefore, exploring essential mechanism of metal precursor-fuel interaction during the combustion process at high temperatures and high self-heating rates is an important fundamental issue that gives a comprehensive knowledge for development and control of distribution of dopants.

The aim of this work is twofold: (i) to develop Ni-based catalyst on a mesoporous network of highly aligned alumina nanofibers (MAN) by wet-combustion method; and (ii) to study the effect of fuel on the combustion mechanism and as-synthesized product by High-Speed Temperature Scanning (HSTS) technique. The HSTS allows fast heating

**Table 1**

The combustion enthalpy of the fuels, and the molar ratio of nickel nitrate to fuel.

Fuel	$\Delta H_c$ , Kcal/mol	$\nu_{Ni(NO_3)_2} / \nu_{fuel}$	$\Delta H_c$ of the added fuel, Kcal
Glycine	230.9 [23]	1.1	254
Urea	150.9 [24]	1.67	252
Citric acid	486.5 [25]	0.52	253

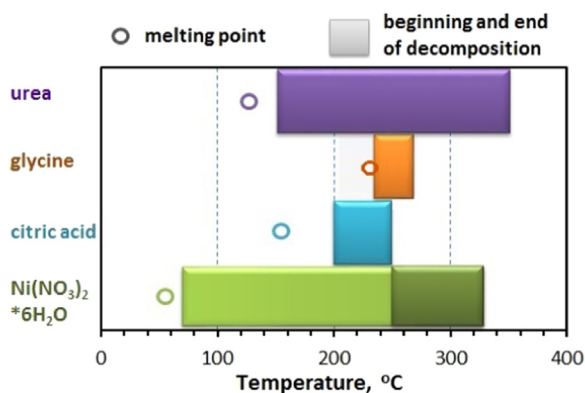
the samples (up to  $10^4$  °/min) up to real solid-state combustion conditions, which is reported to be around  $10^2$  °/min, and studying mechanism of the process [14–16]. However, there is no attempt to study the mechanism of liquid based processes; particularly, solution combustion method. The HSTS is used to reveal the mechanism and kinetics of the combustion processes; moreover, due to the high heating-cooling rates, the HSTS performs interrelated in situ and *ex situ* measurements (XRD, SEM, TEM, etc.) via quenching the samples ( $V_q \sim 12\,000$  °/min) at different stages of the process. In addition, this technique allows studying the dynamics of the phases, evolution of the morphology and structural transformations in the real-time and working conditions. For the first time the technique was used for thorough examination of the solution-based combustion process using the mesoporous substrate immersed with a reactive solution.

## 2. Experimental

All reagents, nickel nitrate hexahydrate (> 98.5%, Lach-Ner), urea (> 98%, Sigma), glycine ( $\geq 99\%$ , Sigma) and citric acid (> 99%, Sigma-Aldrich), were analytical grades and used as received.  $Ni(NO_3)_2 \cdot 6H_2O$  was used as a source of metal and oxidizing agent; whereas urea, glycine and citric acid were used as fuels. The mesoporous network of alumina was used as a carrier. The morphology of the alumina fibers are illustrated in the co-authors previous work [17]. The BET surface area and XRD pattern and the of the mesoporous alumina network used are provided elsewhere [10,26].

To prepare the reactive solutions, 2.91 g of  $Ni(NO_3)_2 \cdot 6H_2O$  and 0.83 g of glycine, 1 g of urea or 1 g of citric acid were dissolved in 5 ml of deionized water. The amount of fuel was calculated to provide similar amount of energy (combustion enthalpy ( $\Delta H_c$ )) to the reactive solution (Table 1).

The obtained homogeneous aqueous reactive solutions were dropped onto 1 g of alumina nanofibers, which subsequently were placed in a muffle furnace preheated to 400 °C in order to heat the sample as fast as possible and to ensure fast elimination of the gases, which could prohibit agglomeration of the particles. The process was accomplished in 30 min. The schematic representation of the method, which is essentially a combination of sol-gel, dip coating and combustion synthesis, is illustrated in Fig. 1.



**Fig. 2.** Coverage of decomposition temperatures and melting points of precursors. The decomposition range and the melting points of the reagents illustrated according to the literature data [19–22].

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