Combustion synthesis of spinel materials for catalytic applications

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ABSTRACT

Spinel mixed zinc ferrite materials (M^{2+}Zn^{2+}Fe_2O_4, where M=Mn, Ni) were synthesised via self-propagating high-temperature synthesis (SHS) combustion reactions in the solid (SPSHS) and in the liquid phase (LPSHS), to be used as high-temperature redox catalysts for water splitting and production of hydrogen. In the SPSHS route, combustion reactions between metal/oxide powder mixtures and oxygen were employed, whereas in the LPSHS route the precursors were metal nitrates and glycine (CH_2COOHNH_2). The effects of reactants stoichiometry (fuel/oxidizer/moderator ratios, oxygen source) on the combustion characteristics and on products’ phase composition and properties were studied. By “fine-tuning” the synthesis parameters, products from single-phase, pure and well crystallized spinel (M_xZn_{1-x}Fe_2O_4 to the divalent iron doped oxide (M_xZn_{y'}Fe_{1-x'-y'})O could be controllably synthesized. Catalytic experiments have demonstrated that combustion-synthesized powders manifest increased catalytic activity compared to similar products obtained by “conventional” solid state sintering.

INTRODUCTION

Spinel materials (AB_2O_4) are widely employed in high-temperature catalytic applications such as desulfurization [1], steam reforming [2] etc. because of their high thermal stability. Among the ferrites, Zinc spinel ferrites, known as an important technological class of magnetic materials since several decades ago, have recently received renewed interest since they have demonstrated potential for catalytic water splitting and production of hydrogen [3,4]. Currently, the worldwide production of these materials on a large scale is taking place by the typical ceramic process that involves mixing of the precursor oxides (or carbonates), pre-firing at temperatures around 900 °C, fine-milling, addition of dopants, spray-drying, cold compaction and shaping by cold-pressing and finally firing at temperatures of the order of 1200-1300 °C for several hours under controlled oxygen partial pressure. Because of the long reaction times that are common in reactions between solids, several alternative techniques for the synthesis of ferrite powders have been developed recently, employing either solid or liquid precursors. Self-propagating High-temperature Synthesis (acronym SHS), proposed by Merzhanov and co-workers in the former Soviet Union at the late 1960’s [5] is one of the most attractive synthesis routes for these materials and has recently received considerable attention since it is characterized by very short synthesis times without the requirement of the “classic” sintering at high temperatures. The SHS process has been thoroughly investigated for the preparation of Ni-, Li-, Mg-, Sr- barium hexaferrites [6-8] but much less extensively for the synthesis of Mn/Ni-Zn-ferrites. In this study, Mn- and Ni-doped Zn ferrites were synthesized via Combustion reactions both in the solid and in the liquid phase. Solid Phase Self-propagating High-temperature Synthesis (SPSHS) is based on the heat released from the reaction of iron metal powder (“fuel”) with oxygen (“oxidizer”) in the presence of the dopant...
metal oxides (MnO, NiO, ZnO), whereas Liquid Phase Self-propagating High-temperature Synthesis (LPSHS) on the reaction of nitrate salts Me_{x}(NO_{3})_{y} ("oxidizer") with soluble organic substances that contain amino-groups ("fuel") (glycine in the present study) to form ammonium nitrate that is explosive and in addition, stable chelates with the metal ions in solution, preventing selective precipitation before combustion. The synthesized products were comparatively characterized with respect to phase composition, morphology and activity towards the water-splitting reaction.

EXPERIMENTAL

SPSHS: Doped-ferrites corresponding to the general composition (Mn/Ni)$_x$Zn$_{1-x}$Fe$_2$O$_4$ were synthesized using metal Fe and MnO or Mn$_3$O$_4$, NiO, ZnO and Fe$_2$O$_3$ as reactants. The latter acts as a “thermal ballast/moderator” to control the synthesis temperature. The general reaction scheme can be described as [7]:

$$2k \text{Fe} + (1-k) \text{Fe}_2\text{O}_3 + x \text{AO} + (1-x) \text{ZnO} + w \text{NaClO}_4 + (1.5k - 2w) \text{O}_2 \rightarrow (A_x\text{Zn}_{1-x})\text{Fe}_2\text{O}_4 + w \text{NaCl}$$

...(1)

where A represents Mn or Ni. As indicated by Eq. (1), NaClO$_4$ was occasionally added to the mixture as an additional solid-source oxidizing agent [7]; the produced NaCl was removed easily by washing the powder with water. The reactant oxide powders and iron metal were dry-mixed and subsequently poured in a Mo boat (Fig. 1a) based on the “filtration combustion” configuration described elsewhere [9], with dimensions ca. 1cm, width of ca. 3cm and length of ca. 10cm. The boat was placed in a properly equipped SHS reactor [10]; ignition was achieved with the aid of a W filament immersed at one edge of the powder bed; propagation was recorded via an infrared camera (FLIR ThermaCAM SC2000) mounted on a ZnSe window on the top of the reactor chamber and stored in electronic format. A sequence of frames from a typical IR video thermogram describing steady flame propagation (i.e. a reaction front with constant shape moving ahead with constant velocity) is shown in Figs. 1b,c. Under this propagation mode all the reactant “sees” essentially the same temperature conditions and the product is much more homogeneous and uniform. Temperatures in excess of 1000 °C were achieved, whereas the synthesis times were of the order of few seconds. The reaction continues after the passage of the flame front, in the so-called “afterburning” stage where essentially proceeds to completion.

LPSHS: The required proportions of Fe(NO$_3$)$_3$*9H$_2$O, Mn(NO$_3$)$_2$*4H$_2$O, Zn(NO$_3$)$_2$*6H$_2$O were dissolved in water, glycine (CH$_2$COOHNH$_2$) was added and the solution was slowly heated at 70-80 °C to form a viscous gel which upon further heating dissociated violently producing a high-temperature flame with the aid of which the metal ions reacted with oxygen to the respective oxide powders that are ejected from the beaker in the form of glowing dendrites (Figs 1d-f) The respective reaction scheme for the case of (Total metal atoms/moles of glycine = 1/1) is shown below:

$$2\text{Fe(NO}_3\text{)}_3+x\text{Mn(NO}_3\text{)}_2+(1-x)\text{Zn(NO}_3\text{)}_2+3\text{NH}_2\text{CH}_2\text{COOH} \rightarrow (\text{Mn}_x\text{Zn}_{1-x})\text{Fe}_2\text{O}_4 + 6\text{CO}_2 + 5.5\text{N}_2 + 7.5\text{H}_2\text{O}$$

...(2)

The SHS powder products were subsequently ball-milled using water and steel balls. Structural characterization of the powders was performed by X-Ray Diffraction analysis (XRD) using a Siemens D-500 Kristalloflex X-ray powder diffractometer. Particle size analysis was performed with laser scattering (Malvern Mastersizer) on dispersions of the powder samples. Microscopic investigations were performed with a JEOL-6400 Scanning Electron Microscope. Catalytic characterization was performed in a U-shaped reactor placed in a Temperature Programmable furnace – the procedure has been described in detail in [11].
RESULTS-DISCUSSION

**Effect of oxygen source**

**SPSHS:** A very important parameter is the nature of “oxygen source” (oxidising agent). Experiments on the synthesis of ferrites via the scheme (1), with reactants corresponding to the synthesis of Mn0.5Zn0.5Fe2O4, under air at atmospheric pressure have shown that for k values lower than 0.5 (ratio of reactant Fe powder (“fuel”) to Fe2O3 (“moderator”) = k/(1-k)), ignition and propagation cannot be achieved with the aid of gaseous oxygen alone at atmospheric pressure. In one hand the amount of gaseous oxygen present in the voids of the powder bed is not enough for complete reaction and on the other hand the pressure gradient between the surrounding atmosphere and the reaction front (where the oxygen gets depleted) is not sufficient to “filter” enough oxygen to the reaction front. Therefore oxygen in the solid phase is necessary to sustain the reaction and lead to self-propagation. If the Fe is in excess with respect to moderator (k higher than 0.7) the reaction can proceed in the absence of NaClO4; however both the propagation velocity and combustion temperature are very low, propagation is unstable and very close to extinction. XRD diffraction in this case shows that the a major part of the powders reamains unreacted - the products consist of free Fe, Fe2O3 ZnO and Mn3O4 and a minute amount of ferrite.

**Effect of reactants stoichiometry**

**SPSHS:** The effect of the ratio of reactant Fe powder to Fe2O3 “moderator” (k/(1-k)) and of the oxygen content, on the phase composition of the products is shown in Fig. 2a (for reactants stoichiometry corresponding to the synthesis of Mn0.5Zn0.5Fe2O4). Low values of the (fuel/moderator) ratio (k=0.3) are not sufficient to complete the reaction, and thus the product contains still unconverted reactants. An “intermediate” value of the (fuel/moderator) ratio (k=0.5) favors the formation of single-phase ferrites, whereas a high value (k=0.9) favors the formation of the “least-oxygen-containing” phase (MxNyFe1-x-y)O provided though that the amount of oxygen is low enough (reaction under vacuum) to suppress melting of Fe. The important conclusion here is that by carefully controlling the exothermicity of the reaction via the amount of “fuel” (Fe) and “oxidizer” (oxygen), a whole range of different products can be synthesized with the same experimental configuration: from “pure”, well-crystallized ferrite phase MxN1-xFe2O4 to the oxide of divalent metals (MxN1-xFe2O4).
**LPSHS:** The effect of the molar ratio of metal nitrates (oxidizer) to organics (fuel), on the products phase composition is shown in Fig. 2b. The reaction conditions favor the formation of single-phase Mn$_x$Zn$_{1-x}$Fe$_2$O$_4$, poorly or strongly crystallized depending on the (fuel/oxidizer) ratio. For the ratio (1/1) the reaction proceeds with a bright flame and violent expulsion of gases (Fig. 1d) within few seconds, whereas very high product yields - of the order of 92% of theoretical - were obtained. The product dendrites were soft and friable and consist of very well crystallized ferrite (Fig. 2b). Higher ratios (2/1, 3/1) affect the combustion mode: combustion takes place in the “smoldering” rather than the “explosion” regime, proceeding much more slowly, without a bright flame and resulting in much less-crystallized products.

**Fig. 2**  
(a) SPSHS: Effect of (fuel/moderator) ratio on products’ phase composition, (b) LPSHS: Effect of (fuel/oxidizer) ratio on products’ phase composition

**Effect of kind and stoichiometry of dopant metal**

**SPSFS:** Fig 3a shows the effect of the divalent dopant metal on front propagation velocity and on combustion temperature. There is no dependency of the front velocity; however combustion temperature increases in the order Fe<Mn<Zn≈Ni in analogy with conventional powder synthesis, where the reaction between ZnO and Fe$_2$O$_3$ for the formation of ZnFe$_2$O$_4$ takes place at lower temperatures than the corresponding reactions with MnO or NiO.

A whole range of Ni-Zn ferrites (Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$) was synthesized with k=0.5, with various relative percentages of the two dopant metals (x=0, 0.2, 0.5, 0.8, 1). The effect of Ni stoichiometric coefficient on the combustion characteristics is shown in Fig. 3b. It can be seen that the relative amount of the two dopant metals affects the front velocity but much less the combustion temperature.

**Fig. 3**  
(a) Effect of (a) the kind of dopant metal and (b) of the relevant amount of Ni, Zn dopants on combustion characteristics
The presence of a divalent metal oxide is necessary for the synthesis of spinel phase. Irrespective on whether either one of NiO, MnO or ZnO or their mixtures were used to react with Fe in the presence of Fe₂O₃, the product was always single-phase ferrite. When no dopant oxide was used and therefore no divalent cation was present in the reaction of Fe with Fe₂O₃ even though combustion temperature was similar to the cases with dopant oxides, propagation velocity was much lower and the product was Fe₂O₃ instead of FeFe₂O₄. With any kind of divalent dopant metal (Ni, Mn, Zn) the product was single-phase ferrite (Fig. 4a).

**LPSHS:** The same effect was observed in the LPSHS route. From the two typical XRD spectra shown in Fig. 4b, it can be concluded that the presence of a divalent metal is necessary for the synthesis of the spinel phase; otherwise the product is the oxide of the trivalent iron Fe₂O₃. However, since these reactions took place always under open air, no evidence of the formation of the “least-oxygen-containing” FeO phase was observed under any reactants stoichiometry.

**Product morphology, particle size and specific surface area**

Typical SEM photos of SHS products are shown in Fig. 5. Particles synthesized from SPSHS form dense, sintered grains (Fig. 5a), that essentially consist of smaller grains of the order of 1 µm. (Fig. 5b). The mean particle diameter of the as-synthesized products is ≈ 60 µm. “As-synthesized” powders from LPSHS form large agglomerates of the order of 50 µm, full of pores due to the violent expulsion of gases (Fig. 5c). Larger magnifications (Fig. 5d) reveal that these agglomerates consist of much smaller particles with dimensions of the order of few tens of nanometers (50-100 nm).

**Fig. 4** Effect of divalent dopant metals on products’ phase composition for the case of SPSHS (left) and LPSHS (right).

**Fig. 5** Morphology of synthesized products (a), SPSHS, (b) magnification on (b), (c) LPSHS, (d) magnification on (c).

Powders from the two synthesis routes are compared with respect to their mean particle diameter and specific surface area after milling for 9 and 36 hrs in Table 1. SPSHS powders
are coarser and have lower surface area than their LPSHS counterparts (5-7 vs. 19 m²/gr). Milling for 36 hrs reduces the mean particle size down to 5 µm for the SPSHS powders and to 0.5 µm for the LPSHS ones.

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<tr>
<th>Product and Synthesis route</th>
<th>After grinding for 9 hrs</th>
<th>After grinding for 36 hrs</th>
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<td>D₅₀ (µm)</td>
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| (MnxZn₁₋ₓFe₁₋ₓ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋₢₋ₚ₋₢₋ₚ₋₢₋ₚ₋ₚ₋₢₋ₚ₋₢₋ₚ₋ₚ₋₢₋ₚ₋₢₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋ₚ₋₢₋ₚ₋ₚ₋₢₋₢₋ₚ₋₃₋ₚ₋₢₋ₚ₋₃₋ₚ₋₢₋ₚ₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋ₚ₋ₚ₋ₚ₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢₋₢_-
CONCLUSIONS

MnZnFeO powders of a wide spectrum of phases could be controllably produced via the SHS process in the solid and the liquid phase. The flexibility of the synthesis methods was demonstrated: by carefully controlling the exothermicity of the reactions via the amount of “fuel”, “oxidizer” and “moderators”, a whole range of different products can be synthesized: from “pure”, well-crystallized doped spinel ferrite \( M_x\text{Zn}_1-x\text{Fe}_2\text{O}_4 \) to “oxygen-lean” doped wustite \( (M_x'\text{Zn}_y'\text{Fe}_{1-x'-y'}\text{O})_\text{O} \), with the same experimental apparatus. The synthesis reactions can be performed in a simple experimental configuration, easily amenable to scale-up, within very short synthesis times, and with high energy efficiency, avoiding the need for long-term high-temperature post-annealing.

The powders synthesized were evaluated with respect to their catalytic activity for water splitting and \( \text{H}_2 \) production. SHS-produced powders could split water at temperatures as low as 800 °C, giving \( \text{H}_2 \) as the only product. The catalytic activity depends on the amount of divalent iron in the product powder, which in turn is favored by oxygen-lean synthesis atmospheres. Only doped wustite powders \( (M_x'\text{Zn}_y'\text{Fe}_{1-x'-y'}\text{O})_\text{O} \) were efficient water-splitters; doped spinel powders of the type \( M_x\text{Zn}_1-x\text{Fe}_2\text{O}_4 \) synthesized either from solid or liquid precursor materials exhibited negligible catalytic activity because of their lower percentage of divalent iron. For the particular system, further experiments are under way to optimize the kind of dopant divalent metals (Ni, Mn) and their relevant stoichiometry, whereas combustion synthesis of other spinel systems for high temperature catalytic applications \( (\text{MgAl}_2\text{O}_4, \text{CaAl}_2\text{O}_4) \) is under progress.

ACKNOWLEDGEMENTS

The work has been funded in part by the European Commission within the Project “Catalytic monolith reactor for Hydrogen generation from solar water splitting-HYDROSOL” (ENK6-CT-2002-00629), under the ‘Energy, environment and sustainable development (part b: Energy)’ Programme (1998-2002). The contribution of Dr. L. Nalbandian, CERTH/Cperi, for performing the catalytic testing experiments is greatfully acknowledged.

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