Synthesis of Ca-doped Spinel by Ultrasonic Spray Pyrolysis

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Abstract

MgAl₂O₄ is a stable catalyst support with potential for replacing gamma-alumina in several applications. However, synthesis of magnesium spinel requires elevated temperatures to avoid phase separation (in MgO and Al₂O₃) at low temperatures, leading to coarsening and reduction of active surface area. In this work, nano CaO-doped and undoped magnesium aluminate were successfully prepared by Ultrasonic Spray Pyrolysis (USP), using a simple adapted experimental set-up operating at 1100°C. During the process, the particles stay at high temperatures for a short period of time, allowing phase stability and limited coarsening. The influence of calcium oxide on the particles morphology and structure was investigated via X-ray diffraction, N₂ adsorption, X-ray fluorescence, scanning electron microscopy and transmission electron microscopy. The spinel nanopowders were obtained as spherical porous agglomerates of ~1 µm. The resulting powder showed low

crystallite sizes in the 5–10 nm range and high specific surface area from 110.0 to 76.6 m².g⁻¹.

Keywords: microstructure, catalyst support, ultrasonic spray pyrolysis, spinel, magnesium aluminate, MgAl₂O₄

1. Introduction

Magnesium aluminate (MgAl_2O_4 , also known as spinel) is primarily used as a refractory material [1-3] and has great potential as a transparent lightweight armor [4]. MgAl_2O_4 possesses superior mechanical properties, such as high elastic modulus (273 GPa) and flexural strength (110 MPa), associated with low density (3.58 g/cm^3), low reflection index (1.736), high optical transmission in visible and mid-wavelength infrared spectra (0.2- $5.5 \mu\text{m}$), and no optical anisotropy due to its cubic structure [5]. MgAl_2O_4 is isostructural to gamma-alumina, and so suitable for catalytic applications [6-9] but with the advantage of being more stable at high temperatures, since transition to alpha phase is not a concern.

Spinel nanoparticles have been previously prepared by different methods [6]. However, a continuous, scalable, and versatile process for the preparation of doped MgAl_2O_4 still remain as a challenge for expanding applications. Among the usual synthesis routes used to produce nano-oxides, Ultrasonic Spray Pyrolysis (USP) has been successfully employed to synthesize nanoparticles as solid and hollow spheres, nanowires, nanoribbons and nanorods [10-14]. In this work we demonstrate the potential of USP to produce doped spinel in a continuous setup. Porous micrometric spheres of CaO-doped MgAl_2O_4 with crystallite size in the range from 5–10 nm and specific surface areas from 76 to $101 \text{ m}^2\cdot\text{g}^{-1}$ were produced as soft spherical agglomerates of $\sim 1 \mu\text{m}$.

2. Experimental

2.1. Powder synthesis

Aqueous solution ($0.1 \text{ M Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $0.2 \text{ M Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was doped with appropriate quantities of hydrated $\text{Ca}(\text{NO}_3)_2$ (all used reagents from Synth Ltda.). A

commercial ultrasonic nebulizer (Britânia – 5L) was used to spray the solutions into a tubular furnace (Lindeberg Blue - 1 m long) with a 0.2 m isothermal temperature zone at 1100°C. The resulting powder was deposited in a glass tube at the end of the tubular furnace. The spinel powder was recovered from the glass tube wall with ethanol and then dried at 100°C. The schematic presentation of the adapted USP system is shown in Fig. 1.

2.2. Characterization

The powder was characterized by specific surface area (SSA) measurements (Micromeritics Gemini III 2375 Surface Area Analyzer) and by X-ray diffraction (X-ray Diffractometer MPD 1880 with Cu K α radiation). From the X-ray diffraction results, the crystallites diameters (d) were estimated by Scherrer's equation using the full width at half maximum (FWHM) of the most intense peak (311). The chemical composition of the products was analyzed using an X-ray fluorescence spectrometer (PANalytical MagixPro), the powder microscopy using a Scanning Electron Microscope (Philips XL 30). Powders were examined by transmission electron microscopy (JEOL 2100, Peabody, MA) at 200 kV. The samples were dispersed in ethanol and deposited on a lacey carbon grid.

3. Results and Discussion

The MgO, Al₂O₃ and CaO contents were determined by XRF (Tab. 1) on the samples produced from the USP reactor. The (MgO+CaO)/Al₂O₃ ratio is close to unit, suggesting the synthesis allowed effective incorporation of all elements.

Fig. 2 shows the XRD patterns of Ca-doped MgAl₂O₄ powders prepared by USP which could be indexed as spinel structure (JCPDS card 05-0672) for all calcium

concentrations. CaO as a second phase was only detected for the sample doped with the highest CaO content (7.3 mol%). No significant lattice parameter change was observed for all CaO amounts. However, the peaks broadening were observed and consistent with crystallite size decreasing. The crystallite sizes were in the 5–10 nm range (Tab. 1), with a non-negligible decrease with increasing CaO concentration. Similar behavior has been previously observed for a large number of systems and different chemical synthesis processes and is likely associated with the dopant segregation onto nanopowders surfaces, with the consequent kinetic reduction of particle growth due to the surface energy decrease [15-17].

The relatively high SSA values are in accordance with the small crystallite sizes (Tab.1). However, the SSA is observed to decrease with increasing CaO content, in contrast to the crystallite size trend. This is likely due to partial sintering during USP, leading to grain boundary formation and consequent surface area decrease. CaO is a very efficient additive for MgAl_2O_4 sintering [18, 19], and should allow sintering activation at the used USP temperature (1100 °C).

The nanocrystals of MgAl_2O_4 were formed after evaporation of the solvent from the solution droplets and the subsequent decomposition of precursors. Therefore, it is expected that the agglomeration of nanoparticles preserve the sphericity of the droplets. The MgAl_2O_4 agglomerates are spherical as observed by SEM (Fig. 3). In contrast to the crystallite sizes, the agglomerate sizes seem to be independent of the CaO concentration and the size distribution seems to be very similar (Fig. 3). This suggests that the chemistry of the liquid precursor does not affect significantly the size of the droplets generated by the nebulizer.

TEM images of the undoped MgAl_2O_4 nanoparticles agglomerates are shown in Fig. 4. The translucence of TEM images indicates that the spherical agglomerates of nanocrystals have a high fraction of porosity – a feature of interest in a heterogeneous catalysis support since it allows gases and liquids to interact with internal surfaces.

4. Conclusions

CaO-doped MgAl_2O_4 nanopowders were successfully prepared from precursor nitrates solutions by Ultrasonic Spray Pyrolysis (USP) at 1100 °C. The spinel nanopowder was produced as spherical agglomerates with approximately 1 μm size, which is specially suitable for catalyst support applications. The size was essentially independent on the additive concentration. However, CaO reduces simultaneously the crystallite size and specific surface area, probably due to the initial sintering of nanoparticles with the consequent formation of agglomerates with stable microspheres suitable for catalyst support materials.

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Fig. 1 – Schematic presentation of the USP system.

Fig. 2 – X-ray diffraction spectra of Ca-doped MgAl_2O_4 prepared by USP at 1100 °C.

Fig. 3 – SEM micrographs of as-prepared powders with 0.0 (a), 1.4 (b), 3.7 (c) and 7.3 (d) mol% CaO.

Fig. 4 – TEM micrographs of as-prepared powders with 0.0 mol% CaO.

Table 1 – Chemical composition, crystallite size and specific surface area of CaO-doped MgAl_2O_4 powders prepared by USP at 1100 °C.

Target concentration (mol% Ca)	Final CaO molar %	$\text{Al}_2\text{O}_3/(\text{MgO} + \text{CaO})$	Crystallite Size (nm)	SSA (m^2/g)
0.0	0.0 ± 0.1	1.0	9.5 ± 0.2	101.0
2.0	1.4 ± 0.1	1.1	6.9 ± 0.2	101.5
5.0	3.7 ± 0.1	1.1	6.5 ± 0.2	81.1
10.0	6.9 ± 0.1	1.0	5.2 ± 0.2	76.6

Fig. 1

Fig. 2

Fig. 3

Fig. 4