Synthesis of stoichiometric nickel aluminate spinel nanoparticles†

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ABSTRACT

Nickel aluminate is a transition metal oxide with spinel structure with potential applications as catalysts and sensors. Both applications benefit from high specific surface areas as well as chemical stoichiometry control. However, a systematic approach to understand synthetic parameters affecting stoichiometry and agglomeration of nickel aluminate nanoparticles is still lacking. In this work, co-precipitation using direct and reverse strikes and polymeric precursor techniques were comparatively studied to address this problem. While the polymeric method could deliver stoichiometric spinel, the samples were highly agglomerated exhibiting low surface area. Both co-precipitation procedures produced smaller sizes and less agglomerated nanoparticles as compared to the polymeric precursor, but for the reverse-strike, Ni²⁺ preferentially formed a soluble complex with ammonia and led to nickel deficient nanoparticles. Stoichiometric (1 mol NiO:1 mol Al₂O₃) nanocrystalline nickel aluminate was only achieved when using controlled excess Ni²⁺. The normal-strike lead to more stoichiometric compositions without need for excess cations, but the obtained nanoparticles were less homogeneous and showed smaller surface areas as compared to the reverse-strike method.

Keywords: Spinel, nickel aluminate, nanopowder, stoichiometry

INTRODUCTION

Aluminate spinels generally present high thermal stability and melting points, mechanical stability, and resistance to alkalis and acids (Zawadzki and Wrzyszcz 2000). In particular, due to its defect chemistry, nickel aluminate is being considered in catalytic applications and proposed as a candidate material in high-temperature fuel cells (Kou and Selman 2000). NiAl₂O₄ is also a potential candidate in metal-ceramic composite because of its excellent strength and wettability with metal (Kim et al. 2000). In these applications, nano-sized particles are preferable as they can provide higher surface areas. Moreover, highly stoichiometric compositions are also of interest for those applications as are associated with higher melting points as compared to non-stoichiometric ones. Stoichiometry has also been shown to be of important for studies of relative stabilities of cations in octahedral and tetrahedral sites (Cooley and Reed 1972); and studies of applications in radiation environments, given that stoichiometric spinels are more resistance to radiation damage than non-stoichiometric ones (Sickafus et al. 1996).

Several synthesis methods have been reported to obtain crystalline NiAl₂O₄ spinel with nano-sized particles (Cesteros et al. 2000; Clause et al. 1992; Deraz 2013; Kiminami et al. 2005; Mohammadpour Amini and Torkian 2002; Nazemi et al. 2012; Nogueira et al. 2007; Platero et al. 1999;Suciu et al. 2006). Among them, sol-gel method, using alkoxides as the precursor, was able to produce nanoparticle with particularly high surface area (Platero et al. 1999). But the cost of alkoxides and the by-products of this method limit its engineering applications (Jeevanandam et al. 2002). Pechini method (Pechini 1967), also known as modified sol-gel method, or polymeric precursor method (Cushing et al. 2004), was also successfully used to obtain highly homogeneous nickel aluminate spinel with small crystallite sizes (Kiminami et al. 2005; Segal 1997). However, it has been recently reported that Pechini method may leave serious carbonate contaminations during synthesis of spinels (Rufner et al. 2013). The contamination is typically located on the surface of the nanoparticles, which can lead to non-stoichiometric spinel structures because the carbonate phase may present a different cationic composition as the oxide. Coprecipitation method using direct strike has been reported to show advantages over the Pechini method in the preparation of MgAl₂O₄ in respect of purity, particle size distribution, and agglomeration. This technique has also been studied to synthesize nickel aluminate spinel (Cesteros et al. 2000; Mohammadpour Amini and Torkian 2002), but while particle size and surface area were reported previously, stoichiometry of the resultant spinel was not checked thoroughly in those studies, leaving several open questions, the main one related to fact that nickel cations can easily form complexes in basic solution, possibly causing non-stoichiometric compounds upon co-precipitation.

In this work, we present an in-depth study of the stoichiometry, size, and agglomeration states of nanoparticles prepared by three different methods: Pechini, reverse-strike co-precipitation, and normal-strike co-precipitation. The goal is to identify the more adequate method to produce stoichiometric, size-controlled, and non-agglomerated particles by understanding and tuning the physical-chemistry of those methods.