Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Co-Al spinel-based nanoparticles synthesized by flame spray pyrolysis for glycerol conversion

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ARTICLE INFO

Article history:
Received 10 February 2017
Received in revised form 29 September 2017
Accepted 11 October 2017
Available online xxxx

Keywords:
Flame spray pyrolysis
Catalyst
Cobalt
Nanoparticles
Glycerol conversion

ABSTRACT

The catalytic properties of Co-Al spinel nanoparticles prepared by liquid-feed flame spray pyrolysis (L-FSP) were investigated in the glycerol conversion in gas phase in an atmosphere of hydrogen. Reduction at 1123 K of the as-synthesized spinel nanoparticles induced the formation a new phase containing metallic cobalt species. Although, the reducibility of cobalt oxides is greatly decreased due to interaction with aluminium species, this strong interaction may prevent the aggregation of Co particles under the harsh reduction conditions. X-ray photoelectron spectroscopy (XPS) of the reduced spinel nanoparticles at 1123 K revealed that the Co/Al atomic ratio has decreased to Co/Al = 0.11, which may indicate a redistribution of the aluminum and cobalt species at the surface of the sample submitted to the reduction in a flow of hydrogen at 1123 K. X-ray diffraction (XRD) and high resolution electron microscopy (HRTEM) also reinforced the formation of metallic cobalt species after reduction of cobalt from the spinel nanoparticles at 1123 K. The main products obtained from the conversion of glycerol in the gas phase were hydroxyacetone, pyruvaldehyde, lactic acid and lactide. FSP successfully gave insights to ensure uniform dispersion of the active metal on a support material.

1. Introduction

Glycerol is an extremely versatile building block within biorefineries as it offers many opportunities for production of useful chemicals. Nearly two-thirds of the world's glycerol production comes as by-product from biodiesel. Furthermore, biodiesel production increased rapidly from 1 million tons in 2000 to 25 million tons in 2015 [1–3]. Thus, the availability of glycerol is expected to increase as the demand for biodiesel continues to rise globally. Hence, the transformation of glycerol into valued-added products and commodity chemicals has been intensively studied over the last decade [2].

The transformation of glycerol by catalytic conversion is often carried out using noble metal-based catalysts for hydrogen activation. Conversely, transition metal-based materials are alternative catalysts for glycerol transformation [5–7]. Despite their lower activity for hydrogenation compared to noble metals they present other advantages, such as much lower prices and higher resistance to poisoning [8].

In addition to the kind of metal for the catalyst other features must be considered when selecting a material namely, the size of the metal particle, the type and morphology of the support, and the homogeneity of the catalyst and the metal dispersion. Numerous studies have shown that particle size and dispersion of the metal play a major role in the selectivity of catalytic reactions [7]. The dispersion, defined as the fraction of the atoms in a cluster present on the catalyst surface, depends on the conditions of preparation, approaching unity when these metallic clusters are extremely small of the order of 1 nm in size [8]. The control of the size of metal nanostructures may thus provide powerful a method to enhance the catalytic activity of metal particles [9].

Cobalt is one of the most attractive transition metals used in catalytic reactions owing to its availability and relatively low cost [10]. Typically, for heterogeneous catalysis, Co/alumina particles

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https://doi.org/10.1016/j.apt.2017.10.009
0921-8831/

are prepared by using either solid state reactions of their parent oxides (Co_3O_4 and γ-Al_2O_3) or by wet methods (e.g. impregnation, sol-gel process) followed by their thermal treatment in air [11,12]. However, Co_3O_4 and γ-Al_2O_3 have isotype crystal structures that enable the migration of ions from cobalt oxide into the underlying alumina support, thus forming aluminate spinels (e.g., Co_2AlO_4, $CoAl_2O_4$) when heated. It has been suggested that cobalt ions occupying surface octahedral sites of γ-Al_2O_3 are reducible while cobalt ions occupying tetrahedral sites are not reducible at least at temperatures $\leq$ 900 °C [13]. Such preparation methods demand optimization of the metal dispersion on the catalyst and the degree of reduction [14,15]. It is known that Co^{+3} of Co_3O_4 can be gradually replaced by Al^{+3} to produce the series of $Co_{3-s}Al_sO_4$ ($0 < s < 2$) spinels. These series include $CoAl_2O_4$, Co_2AlO_4, Co_3O_4, and more. The interaction between Co_3O_4 and alumina could result in partial substitution of Co^{+3} ions in Co_3O_4 spinel by Al^{+3} ions, thereby hindering the reduction of cobalt species. Cobalt reducibility is known to depend on particle size [16]. The interaction of cobalt species with alumina should also be considered [17]. Alternatively, gas phase methods for cobalt-based catalyst preparation have been explored [18,19].

Gas phase approaches such as the so-called liquid-feed flame spray pyrolysis (LF-FSP) method have been previously used to prepare CoO_x-Al_2O_3 particles [12]. In a FSP system, a metallorganic precursor dissolved in fuel (solvent) is aerosolized into droplets and ignited with a premixed methane-oxygen flame, the organic fuel combusts forming carbon dioxide and water vapor. The metallorganic component forms metal oxide particles. The entire process takes place in a time range of the order of miliseconds. Particles of varying morphologies (solid, hollow, porous, etc.) and sizes can be produced by controlling process parameters [20–22]. Particularly, the flame temperature, the residence time in the flame, and the droplet evaporation time play a key role in the particle formation. In a typical FSP, the droplets may undergo complete evaporation. In such case, the metallorganic precursor's vapor reacts and transforms into metal oxide vapor, which then forms small nanoparticles by homogeneous nucleation [20–22]. Nanoparticles synthesized via FSP exhibit typically small crystalline sizes and high surface areas. Particularly, in the synthesis of metal catalysts, aerosol methods ensure uniform dispersion of the active metal on a support material, unlike conventional wet-based methods. If the size of the metal nanoparticles is sufficiently small, the fraction of its surface atoms increases, thus improving catalyst performance.

In this work, Co-Al spinel nanoparticles were readily synthesized by a one-step FSP method. The approach allows the production of oxide nanoparticles at a relatively high rate. FSP provides an extremely short residence time of flame particles formation typically in the range of miliseconds [23,24]. The particles were subsequently reduced to obtain metallic cobalt species and investigated in the conversion of glycerol in gas phase. Although, the reducibility of cobalt oxides is greatly decreased due to interaction with aluminium species, this strong interaction may prevent the aggregation of Co particles under the harsh reduction conditions. Reduction of cobalt species is determinant for its catalytic performance in the conversion of glycerol.

2. Experimental

2.1. Catalyst preparation

2.1.1. Flame spray pyrolysis

Aluminium acetylacetonate (99%, Sigma-Aldrich) and cobalt acetate (99,995%, Sigma-Aldrich) were used as received. The precursor solution consisted of a mixture of aluminium acetylacetonate (0.078 mol/l) and cobalt acetate (0.017 mol/l) dissolved in a solution containing 73%-v of methanol (J.T. Baker) in ion-exchanged water. The Co:Al ratio in the precursor solution was approximately 0.22.

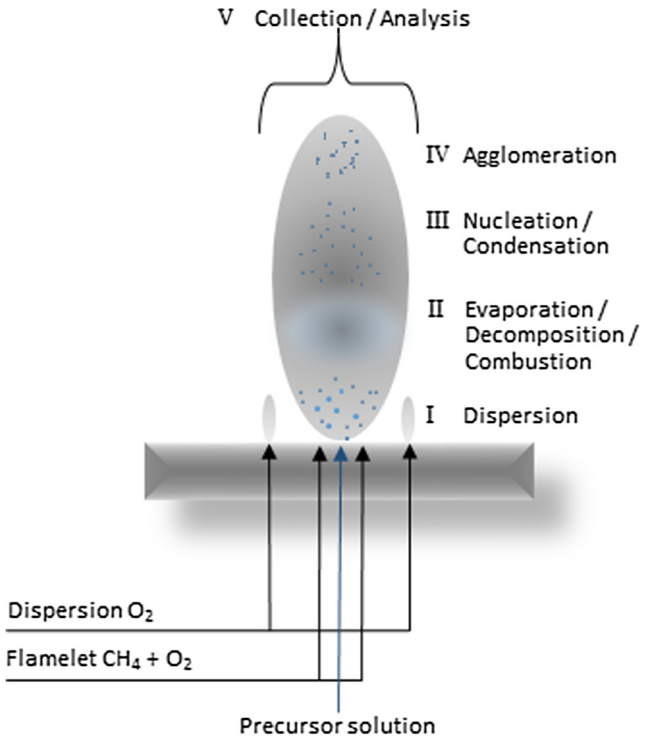

Fig. 1. Schematics of the Flame Spray Pyrolysis system.

Table 1
N_2 physisorption of the as-synthesized Co-Al spinel nanoparticles and Co-Al spinel nanoparticles reduced at 1123 K.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
As-synthesized Co-Al spinel nanoparticles	174	1.21	3.73
Co-Al spinel nanoparticles Reduced at 1123 K	112	0.68	3.69

The flame spray pyrolysis system used for particle preparation has been described previously [25] and is shown in Fig. 1. Briefly, the precursor solution was fed through a capillary at a rate of 5 mL/min and atomized with a high-pressure dispersion gas, O_2, at a flow rate of 5 L/min. A premixed methane-oxygen flamelet with gas flow rates of 1 and 2 L/min, respectively, ignited the atomized precursor solution, resulting in the formation of a high-temperature flame, with temperatures in excess of 2000 K. The produced particles were collected on a Teflon filter (Zefluor, Pall Corporation). Finally, the resultant cobalt sample obtained by flame spry pyrolysis was submitted to reduction treatment. Two reduction temperature treatments were investigated: 723 K and 1123 K. The sample was reduced in a flow of 5% H_2/Ar gas flowing at 20 mL/min for 4 h.

2.2. Catalyst characterization

The morphology and structure of the particles were characterized with a transmission electron microscope (TEM, JEM-2100F, JEOL Ltd.) equipped with a field emission electron source and operated at 200 kV. For the analyses, samples were dispersed in an alcohol and a drop of the suspension was placed over a TEM grid

Please cite this article in press as: A. Lähde et al., Co-Al spinel-based nanoparticles synthesized by flame spray pyrolysis for glycerol conversion, Advanced Powder Technology (2017), https://doi.org/10.1016/j.apt.2017.10.009