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# Effect of preparation conditions on structural and catalytic properties of lithium zirconate

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**Abstract**

Inorganic (inorg) and organic (org) routes with acid (A) and base (B) hydrolyzing agents were utilized to synthesize lithium zirconate (LiZr) nanomaterials. The effect exerted by the nature of hydrolyzing agent and synthesis route on the morphology and structural properties of the samples was studied by X-ray diffraction, Raman spectroscopy, TEM, SEM, XPS, $N_2$-adsorption and $CO_2$-TPD techniques. The characterization results revealed that LiZr-org-B sample prepared using organic base possessed hollow nanospheres which are composed of small platelets; in contrast, LiZr-inorg-B sample prepared using inorganic base showed nanotubular structure due to more alkaline nature of the inorganic precursors. Additionally, LiZr-org samples possessed different textural characteristics and basic properties. LiZr-org samples, in particular LiZr-org-B showed relatively high surface area, uniform micro pores, and more number of basic sites as well as high catalytic activities in transesterification of tributyrin with methanol than LiZr-inorg samples. LiZr-org-B sample is stable and showed excellent reusability for more than five cycles without any loss of activity in transesterification reaction.


*Keywords:* Lithium zirconate; Organic and inorganic routes; Acid and base hydrolyzing agents; Transesterification; Biodiesel

## 1. Introduction

Lithium zirconate ceramic material is a known candidate in fusion reactor designs as a tritium-breeding material due to its excellent stability and tritium release performance at low temperature [1]. The synthesis of lithium-containing ceramic powders has been extensively studied after Nakagawa et al. [2] reported that this material also can absorb a large amount of $CO_2$ based on non-catalytic gas–solid reaction (about 4.5 mol $kg^{-1}$) at high temperature (400–700 °C).

Solid-state reactions between $ZrO_2$ and lithium peroxide (or carbonate) are the best known preparation method to synthesize lithium zirconate powders [3]. In these processes, two precursors are mechanically mixed and treated at high temperatures. Solid-state reactions normally require high temperatures and long reaction times. Ida et al. [4] synthesized lithium zirconate powder with particle diameters larger than 1 μm by solid-state reaction between $Li_2CO_3$ and $ZrO_2$. It was observed that the final particle size of the ceramic powders synthesized by solid-state processes is normally large, partially due to sintering during the high-temperature treatment. In addition, the sublimation of $Li_2O$ cannot be avoided due to high-temperature treatment.

Liquid-phase methods have also been proposed to synthesize lithium zirconate, in which soluble inorganic Zr and Li compounds were used as precursors to obtain a complex solution, which was then dried to form lithium zirconate [5]. Synthesis of pure and homogeneous nanocrystalline ceramic powders from organic precursors is an attractive route. In organic precursor route, formation of hard agglomerates during thermal treatment is expected to be low as the metal atom in the precursor is surrounded by organic moieties. The organic moieties shield the primary oxide particles formed during initial stages of thermal treatment from the neighboring oxide particles [6]. Alvani et al. developed wet chemical routes by

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using metal alkoxides, where temperatures higher than 800 °C were required to synthesize lithium zirconate powder [7]. Montanaro et al. proposed a gelling method using lithium acetate and zirconium propylate as precursors [8]. However, this method yielded particle sizes larger than 40 μm. Ochoa-Fernandez et al. have reported a soft-chemistry preparation route for the synthesis of nanocrystalline lithium zirconate [9]. The authors claimed that the preparation method yields pure nanocrystals of lithium zirconate with pure tetragonal phase using relatively low calcination temperatures.

Khokhani et al. [10] reported sol–gel based synthesis for the preparation of lithium zirconate nanoparticle and sodium doped lithium zirconate nano squares in presence of organic surfactant (CTAB). The same authors also reported non-alkoxide route (using water based sols of inorganic metal salts as a starting reagents) for the synthesis of lithium zirconate nanomaterials.

The depletion of world petroleum reserves and increased environmental concerns have stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy demand [11]. Biodiesel fuel (fatty acid methyl esters), synthesized from vegetable oils, has similar physical properties to petrochemical diesel and is considered the best alternative fuel candidate for use in diesel engines [12]. Biodiesel production involves the catalytic transesterification of long- and branched-chain triglycerides with alcohols to produce monoesters and glycerol [13]. Current syntheses use homogeneous alkaline agents, such as K or Na alkoxides or hydroxides [14]; however, removal of the soluble base after reaction is a major problem, because aqueous quenching results in the formation of stable emulsions and saponification, rendering separation and purification of the methyl ester difficult. As a result, biodiesel production by these routes is still not cost-competitive with petrochemical diesel fuel [15]. Kiss et al. [16] summarized the pros and cons of manufacturing biodiesel via fatty acid esterification using metal oxide solid catalysts. Recently, Grecea et al. [17] developed superior robust super acid catalyst for multiproduct fatty acid esterification. Use of a solid base catalyst offers several process advantages, including the elimination of a quenching step (and associated contaminated water waste) to isolate the products and the opportunity to operate a continuous process [18]. Solid base catalysts including zeolites [19], alkali-metal and alkaline earth metal carbonates and oxides [20], lithium silicates [21], sodium silicates [22], transition metal oxides [23] and layered double hydroxides [24] have been investigated in transesterification reactions. Recently, we synthesized and applied magnesium silicate nanomaterials [25] as catalysts for biodiesel production. However, reports on application of nanocrystalline lithium zirconate as a base catalysts for biodiesel production are scarce. Very recently, Kaur and Ali [26] prepare Li-$ZrO_2$, Na-$ZrO_2$ and K-$ZrO_2$ catalysts for the transesterification of waste cotton seed oil to produce biodiesel. The authors observed the formation of lithium zirconate in case of Li-$ZrO_2$ catalysts and it was able to catalyze simultaneous esterification and transesterification of high free fatty acid containing vegetable oils. However, there is a lack of detailed characterization to correlate the physico-chemical properties of lithium zirconate to its catalytic activity. It is known that preparation conditions and nature of precursors influence the physico-chemical properties such as porosity, surface area, shapes and sizes of nanoporous zirconia [27]. However, to the best of our knowledge, the effect of preparation conditions on the structural and catalytic properties of lithium zirconate nanomaterials has not been reported.

The aim of the present work is therefore, to synthesize lithium zirconate nano powders using inorganic and organic routes with acid and base precipitating agents. The synthesized powders were characterized using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), $N_2$-physisorption and $CO_2$-temperature programed desorption ($CO_2$-TPD) analyses. The physico-chemical properties and catalytic performances in transesterification of tributiryn for biodiesel production were investigated in detail. Furthermore, the reusability of the materials in transesterification reaction was also investigated.

## 2. Experimental

### 2.1. Materials

Zirconyl nitrate [$ZrO(NO_3)_2$], lithium nitrate ($LiNO_3$), zirconyl acetylacetonate [$Zr(C_5H_7O_2)_4$], lithium methoxide ($CH_3OLi$), acetic acid ($CH_3COOH$), nitric acid ($HNO_3$) tetrapropylammonium hydroxide [$(CH_3CH_2CH_2)_4N(OH)$] and ammonium hydroxide ($NH_4OH$) were purchased from Sigma-Aldrich, U.K. All reagents were analytical grade and used as received without further purification.

### 2.2. Synthesis of lithium zirconate nanomaterials

#### 2.2.1. Inorganic route

(1) Acid hydrolysis

In a typical preparation, the stoichiometric amount of reactants, 1 M zirconyl nitrate and 2 M lithium nitrate were dissolved in 300 mL of distilled water. To this solution, diluted $HNO_3$ was added slowly to adjust the pH value of the solution in the range of 1-2. After completion of addition of dil. $HNO_3$, the solution was kept for stirring for 1 hour at ambient conditions, resulting a clear homogeneous solution. Then the solution was kept at 100 °C for gelling and drying for 12 hours. The dried powder was calcined at 700 °C for 4 hours. The sample obtained was designated as LiZr-inorg-A.

(2) Base hydrolysis

In this method, lithium zirconate was precipitated by drop wise addition of ammonium hydroxide to aqueous solution containing stoichiometric quantities of zirconyl nitrate and lithium nitrate. The addition of ammonium hydroxide solution was continued until no more precipitation occurred (pH of the contents was between 8 and 9). Stirring was stopped and the precipitate was filtered and washed with distilled water for five times. The filter cake

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