



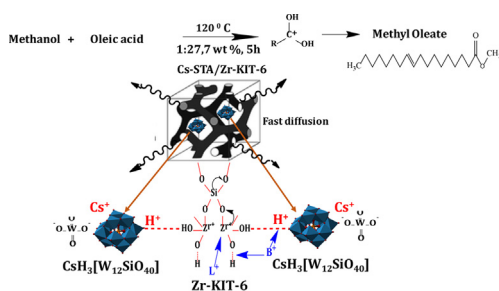
## Full Length Article

## Cs-tungstosilicic acid/Zr-KIT-6 for esterification of oleic acid and transesterification of non-edible oils for green diesel production

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## GRAPHICAL ABSTRACT

Esterification of oleic acid by Cs-STA/ZK.



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## ABSTRACT

The development of solid acid catalyst with superior activity is of high interest for the production of biodiesel. In this study, an attempt was made to synthesize a novel solid acid catalyst based on mesoporous cesium exchanged tungstosilicic acid supported on Zr-KIT-6 (Cs-STA/ZK) and Sn-KIT-6 (Cs-STA/SnK). The catalysts were synthesized by hydrothermal method and characterized by various physicochemical techniques such as PXRD, BET, FTIR, SEM, TEM, XPS, and NH<sub>3</sub>-TPD. The reaction parameters were optimized using Cs-STA/ZK catalyst. The present investigation explores the production of biodiesel from oleic acid and non-edible oils such as castor oil, pongamia oil, and neem oil. Cs-STA/ZK catalyst exhibited the highest conversion in both esterification (99%) of oleic acid and transesterification (98%) of non-edible oils. Further, the recyclability and thermal stability of Cs-STA/ZK catalyst are investigated in detail.

## 1. Introduction

Energy, the key factor of driving force for human life across the globe [1]. Non-renewable fossil fuels are shrinking in quality and quantity slowly. During the past decade, radical development in

metropolitanization and mechanization increased energy scarcity. However, advanced technology and developed scientific methods have reduced the immediate risk of energy inadequacy [2]. In this regard, a greener, renewable and potential alternative to fossil fuel is green diesel which may be synthesized from animal fats, various fatty acids and non-

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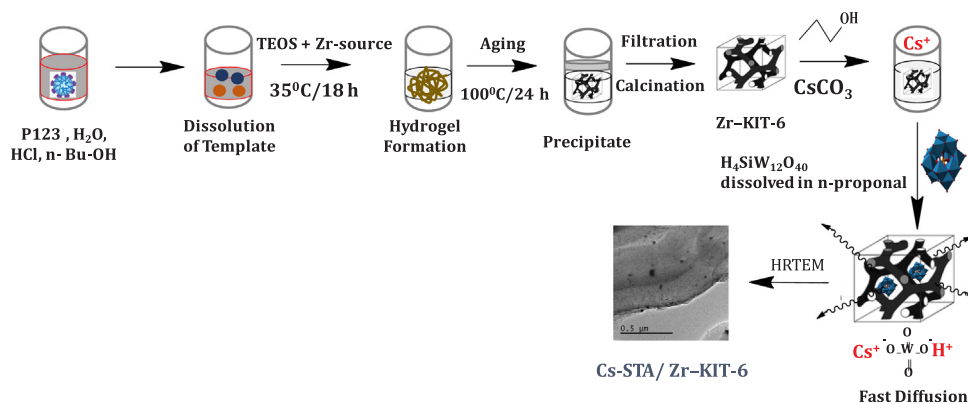


Fig. 1. Schematic diagram of synthetic strategy of mesoporous Cs-STA/ZK.

edible oils through esterification and transesterification [3]. Biodiesel is a methyl ester of fatty acids and triglycerides, which is biodegradable and non-toxic [4]. In biodiesel production, homogeneous catalysts such as  $\text{H}_2\text{SO}_4$  and KOH carry the burden of tedious purification processes, soap formation and generates large amount of wastewater during washing which directly affects the cost [5]. To conquer these issues, various heterogeneous catalysts have been employed due to ease of recycling, ability to withstand high temperature, lack of toxicity, and easy separation [6]. However, the reaction rate of heterogeneous catalysis is lower than homogeneous system due to mass transfer limitations. In this context, porous cubic Ia3d KIT-6 (Korean Institute of Technology) mesoporous silica has proved as a popular candidate, which could provide in-pore accessibility of catalytic acid sites compared to MCM-41 and SBA-15 materials [7]. Modification of such mesoporous materials by active metals incorporation such as Zr, Sn, Ti, etc., is also an important way to improve the catalytic activity [8]. Two important strategies namely “Post-synthesis grafting” which is comparatively difficult and typically results in channel blockage and “Direct synthesis” which is convenient to incorporate hetero metal atoms [9]. Apart from these active metals, another kind of active materials are heteropoly acids (HPA) which are free acidic forms of polyoxometalates and find outstanding applicants among solid acid catalysts. A wide variety of reactions catalyzed by heteropoly acids to offer strong options for clean energy generation compared to usual mineral acids [10–13]. HPA's exhibit considerably superior catalytic activity which has been approximately 1000 times higher than that of  $\text{H}_2\text{SO}_4$  [14,15]. In solid state, HPA's are clean and stronger Bronsted acids than the usual solid acids such as zeolite (H-X & HY), silica-alumina and silica-alumina phosphates. Hence, it is possible to carry out catalytic transformations at lower temperature with less amount of catalyst. Further, heteropoly acids are more desirable while considering safety and ease of handling due to stability and comparatively nontoxic crystalline substances. Despite of these advantages, high solubility in polar solvents, low surface area, and low thermal stability are the major disadvantages of HPA's. HPA's supported with metal oxides such as  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$  and  $\text{Nb}_2\text{O}_5$  are the greatest substitute for simultaneous esterification and transesterification. Recently, Fang Su et al. reported Keggin type HPA's used in homogeneous catalysis for biodiesel production. In addition, they have also been reported for heterogeneously catalyzed biodiesel preparation using  $\text{Cs}/\text{H}_3\text{PW}_{12}\text{O}_{40}$  and supported  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  catalysts [16–18]. The present work focuses on the synthesis of Zr incorporated mesoporous silica (KIT-6) supported with Cs exchanged tungstosilicic acid which is an efficient solid acid catalyst. This work involves the production of biodiesel from oleic acid and non-edible oils using Cs-STA/ZK catalyst. The synthesized solid acid catalyst has interconnected pores, moderate to high concentrations of strong acid sites and hydrophobic surface. The stability and recyclability of catalyst have also been discussed. In addition, there seems to be no reports on the synthesis of mesoporous cesium exchanged tungstosilicic

acid (Cs-STA) supported on Zr-KIT-6 for biodiesel production.

## 2. Materials and methods

### 2.1. Materials

Castor oil, pongamia oil, neem oil were collected from a local farm and used without further treatment. Oleic acid (99%), methanol (99.9%), tri-block copolymer P123 [poly block (ethylene glycol)-poly block (propylene glycol) block-poly (ethylene glycol)],  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (98% purity), Tin (IV) Oxide ( $\text{SnO}_2$ ), cesium carbonate, tungstosilicic acid ( $\text{H}_4\text{W}_{12}\text{SiO}_{40}$ ), tetraethylorthosilicate (TEOS), HCl and sulfuric acid were purchased from Sigma Aldrich and used as such.

### 2.2. Catalyst preparation

Mesoporous Zr-KIT-6 catalysts were synthesized using PEO20PPO70PEO20 (Pluronic P123, Aldrich) as a template by following the methods of Ryoo et al which is shown in Fig. 1.

#### 2.2.1. Synthesis of M-KIT-6 (M = Zr & Sn)

Zr-KIT-6(x) (x = Si/Zr molar ratio) catalyst was synthesized using zirconyl oxychloride octa-hydrate and tetraethyl orthosilicate. The Si/Zr ratio was optimized as 20 from three different ratios such as 20, 50 and 100 which was used in the synthesis [19]. In a representative synthesis, 5.0 g of Pluronic P123 was dissolved in 180 mL of HCl (0.5M) at 35 °C. Then, 5.0 g of n-butanol ( $\text{C}_4\text{H}_{10}\text{O}$ ) was added and stirred for 1 h at 35 °C. At last, 10.6 g of TEOS and necessary amounts of zirconium precursor were added and stirred well for 18 h. Then, the synthesis mixture was transferred to Teflon lined autoclave and kept in an oven at 100 °C for another 24 h. The end product obtained was filtered off followed by washing with distilled water and dried at 100 °C for overnight. The dried catalyst was powdered well and calcined at 550 °C in flowing air for 5 h.

Mesoporous Sn-KIT-6 (x = Si/Sn ratio = 20) catalysts were also synthesized by following the same procedure [19]. During TEOS addition, instead of zirconium precursor, necessary amounts of the tin precursor was added and stirred well for 18 h. Then, the synthesis mixture was transferred to Teflon lined autoclave and kept in an oven at 100 °C for another 24 h. The end product obtained was filtered off followed by washing with distilled water and dried at 100 °C for overnight. The dried catalyst was powdered well and calcined at 550 °C in flowing air for 5 h.

#### 2.2.2. Impregnation of Cs-tungstosilicic acid (Cs/STA)

To avoid the decomposition of Keggin units, the synthesis procedure ought to be carefully planned as the Cs exchanged heteropoly acid was post impregnated on both Zr-KIT-6 and Sn-KIT-6. In a typical synthesis, 0.5 g of Zr-KIT-6 was dispersed on 0.20 g of  $\text{Cs}_2\text{CO}_3$  in 10 mL of n-

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