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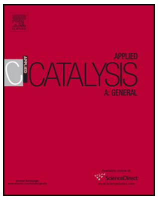

Selective etherification of hydroxymethylfurfural to biofuel additives over Cs containing silicotungstic acid catalysts

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ABSTRACT

A series of Cs exchanged silicotungstic acid (STA) catalysts were prepared and their physico-chemical properties were derived from FT-Infrared, X-ray diffraction, Laser Raman, temperature programmed desorption of ammonia and BET surface area. The characterization results revealed that the Keggin structure of STA remained intact even after Cs ions replaced its protons. The catalysts activity was evaluated for the selective etherification of 5-hydroxymethylfurfural (HMF) with ethanol for the synthesis of 5-ethoxymethylfurfural (EMF). The partial exchange of Cs ions with protons of STA resulted an increase in acidity and the catalysts with two Cs ions in STA showed highest acidity. The activity was explained based on the acidity, surface and structural properties of the catalysts. A detailed study was made on the effect of various reaction parameters such as influence of reaction temperature, reaction time, Cs content on STA to unveil the optimize reaction conditions. The catalyst was recovered easily from the reaction mixture and reused at least four times with constant activity.

1. Introduction

The limited oil resources, as well as economic, geopolitical and environmental reasons indicate that the current petroleum based fuels are unsustainable. Biomass is considered as a sustainable raw material for the production of many chemicals and fuels [1]. Nature produces about 170 billion metric tons of biomass per year by photosynthesis and 75% of which can be assigned to carbohydrates [2,3]. HMF a potential chemical can be obtained from cellulosic biomass such as fructose, glucose, sucrose and inulin [4–7]. HMF can be used to produce 2,5-dimethylfuran (DMF) potential biogasoline compound [8], and 2,5-furandicarboxylic acid (FDCA) a precursor to the polyester, PET [9–11] and 5-ethoxymethylfurfural (EMF), a promising biofuel and fuel additive. Among these chemicals etherification of HMF with ethanol to produce EMF is an important approach as it is an excellent additive for diesel [12]. It has a high energy density of 8.7 $\mathrm{kW\,h\,L^{-1}}$, which is comparable with that of standard gasoline (8.8 $\mathrm{kW\,h\,L^{-1}}$) and diesel fuel (9.7 $\mathrm{kW\,h\,L^{-1}}$), and significantly higher than the widely familiar bio-ethanol (6.1 $\mathrm{kW\,h\,L^{-1}}$) [13]. Avantium has used EMF as a blend for commercial diesel in engine tests and found that the engines ran smoothly. Furthermore, there is less solid contamination and soot [14]. EMF may also be hydrogenated over metal catalysts to yield 5-(hydroxyethyl) furfuryl alcohol, which is much more miscible in diesel and has a similar combustion profile to ethanol [15]. Different methods have been reported for the preparation of EMF. EMF have previously been synthesized via 5-chloromethylfurfural with ethanol [16]. Alternatively, EMF has also been synthesized by direct etherification of HMF with ethanol in the presence of acid catalysts such as Amberlyst-131[17], $H_4SiW_{12}O_{40}$/MCM-41, H_2SO_4 [18], ZrO_2/SBA-15[19], Ag_1TPA [20], 40 wt% MCM-41-HPW [21], Fe_3O_4@SiO_2 [22], graphene oxide [23], silica-SO_3H [24], SO_3H-functionalized polymers [25] and cellulose sulfuric acid catalysts [26]. Even though different heterogeneous catalysts are explored for synthesis of EMF, over most of the catalysts activity is limited. The role of catalysts surface and structural characteristics on the etherification activity of HMF is not studied in detailed. Moreover the influence of reaction parameters and reusability of catalysts are not studied in details.

Heteropolyacids (HPAs) have been widely used in the conversion of carbohydrates, especially in the esterification and etherification reactions because of their Brønsted acidity, high proton mobility and the ability to accept and release electrons [27]. HPAs and their salts are useful acid catalysts for diverse reactions that require strong acidity [28]. Although the acid forms are themselves useful solid catalysts, they are highly soluble and difficult to separate from polar media [29]. HPAs grafting onto high-surface area porous support is often used to enhance their

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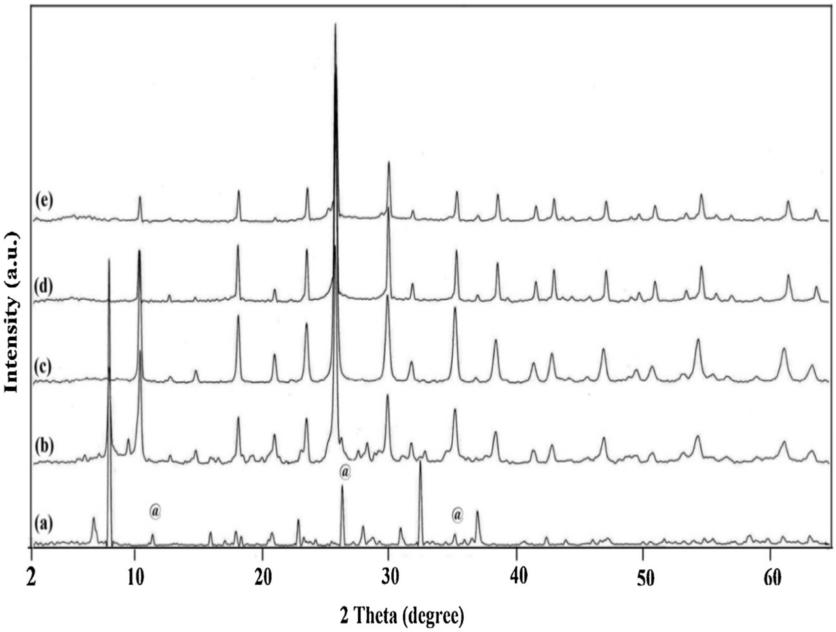

Fig. 1. XRD patterns of CsSTA catalysts (a) STA, (b) Cs_1STA, (c) Cs_2STA, (d) Cs_3STA, (e) Cs_4STA catalysts.

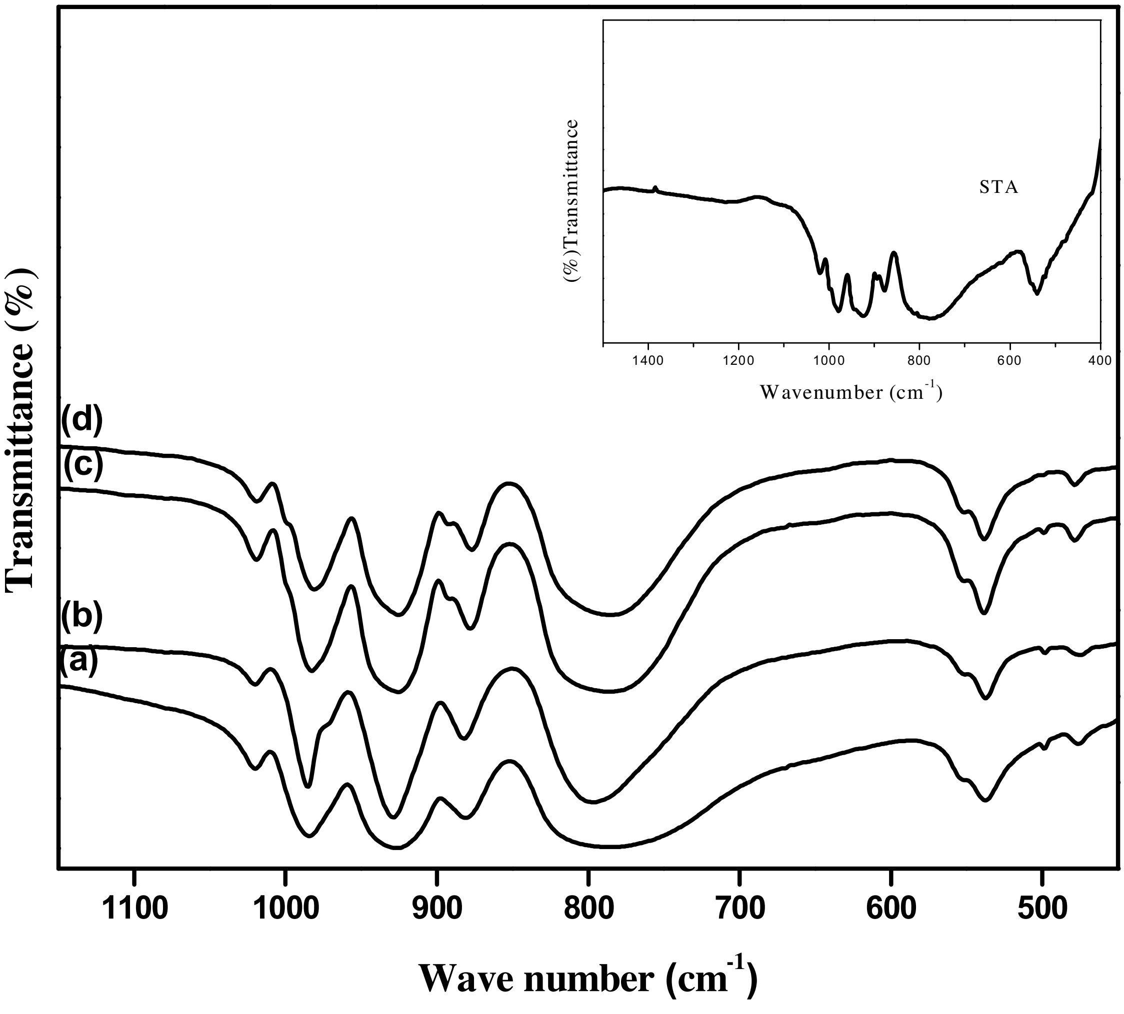

Fig. 2. FT-IR spectra of CsSTA catalysts (a) Cs_1STA (b) Cs_2STA (c) Cs_3STA (d) Cs_4STA, STA (as inserted figure).