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Cs salt of Co substituted lacunary phosphotungstate supported K10 montmorillonite showing binary catalytic activity

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HIGHLIGHTS

- A single catalyst showing diverse role.
- Excellent catalytic activity in eco-friendly environment.
- The catalyst is much tolerable towards the reaction conditions.

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ABSTRACT

The present study explores the fabrication of cesium salt of cobalt substituted lacunary phosphotungstate supported K10 montmorillonite. Lacuna creation in the phosphotungstic acid and cobalt substitution was confirmed from FT-IR spectroscopy. The presence of cobalt in its +2 oxidation state was established from UV–Vis DRS and XPS study. The high acidity of the catalyst was evidenced from NH_3-TPD measurement. Other characterization techniques like XRD, N_2 adsorption–desorption, TG-DTA and H_2-TPR discovered various dimensions relating to the catalyst. This single system, enriched with high acidity and oxidative ability showed superlative catalytic activity in the absence of any solvents towards both esterification of oleic acid with methanol and selective oxidation of benzyl alcohol to benzaldehyde. While giving 94% methyl oleate yield in the esterification reaction, it showed appreciable results toward the oxidation reaction with 91% conversion and 99% benzaldehyde selectivity in just 2 h.

1. Introduction

Montmorillonite has been highlighted prominently in clay-mediated organic synthesis for many years because it is economic and environment friendly [1–6]. It is basically a hydrated 2:1 layered dioctahedral aluminosilicate of the smectite group of clays [7]. It is composed of two tetrahedral silicate sheets which are bonded to either sides of an octahedral aluminate sheet. The charge balancing alkali and alkaline earth metal cations occupies the interlayer space [7].

K10 montmorillonite is commercially available acid activated clay. During its preparation, the acid treatment on natural clay replaces the interlayer cations with protons and the acid leaches Al^{3+} from the octahedral layers. The protons replacing the interlayer cations along with the leached hydrated alumina occupying the cation exchange sites result in an enhanced acidity in K10 montmorillonite [8–14]. The leaching of Al^{+3} from the octahedral layer creates many mesopores resulting in a high surface area material. So the main consequences of acid activation are an increase of surface area, porosity and number of acid sites compared to the natural clay [15]. This makes K10 montmorillonite a very good acidic support. To increase the acidic activity, the acid activated montmorillonite can be modified by pillaring with transition metal oxides or in some other way [16–18].

Another known star in acid catalysis, bearing high acid sites is Cs salt of phosphotungstic acid [19]. A combination of Cs salt of phosphotungstic acid and K10 montmorillonite results in a strong acid catalyst. This material has got enormous attention in the field of acid catalysis [20]. Some structural modifications on phosphotungstic acid skeleton by cleaving one or more of its terminal oxygen–metal units and co-ordinating transition metal ions into the vacant sites makes it a wonderful oxidation catalyst [21]. Therefore, transition metal substituted Cs salt of lacunary phosphotungstic acid promoted K10 montmorillonite can be an effective catalyst towards both the acid catalyzed as well as oxidation reactions. With this thought in mind, we prepared the catalyst and employed it towards both acid catalyzed and oxidation reactions.

We have carried out esterification of oleic acid with methanol and oxidation of benzyl alcohol to benzaldehyde with the help of

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