



Synthesis of hybrid SBA-15 functionalized with molybdophosphoric acid as efficient catalyst for glycerol esterification to fuel additives

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ABSTRACT

Fibrous mesoporous hybrid silica (SBAH-15) with mesopore diameter of 70 Å was synthesized using pluronic P123 (EO₂₀PO₇₀EO₂₀) as surfactant, with Brij S100 as nonionic co-surfactant. Series of catalysts with different molybdophosphoric acid (MPA) loading (5–25%) were synthesized by the thermal decomposition of MPA species in the lattice of SBAH-15. Catalysts calcined at 560 °C undergone a thermal decomposition of MPA resulted in the formation of β-MoO₃ active species. The effectiveness of the hybrid support was evaluated by comparison with analogous catalyst prepared by incorporating MPA into the framework of classical SBA-15. The catalytic performance of the prepared acid catalysts was examined during glycerol esterification with acetic acid. Mono-, di- and triacetyl glycerol (MAG, DAG and TAG, respectively) were the esterification reaction products. SBAH-15(15) catalyst, with 15 wt.% MPA loading, exhibited an excellent activity during this reaction, indicated by the complete glycerol conversion (after 1 h) with a corresponding combined selectivity of 86% toward both DAG and TAG. The best reaction conditions are: reaction temperature of 110 °C, glycerol to acetic acid molar ratio of 1:6 and reaction time of 3 h. The SBAH-15(15) catalyst demonstrated good stability in activity upon recycling for four times.

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1. Introduction

Bio-based fuels are attractive alternatives to fossil fuels due to their environmentally benign and renewable nature. Biodiesel is the most promising biofuel when blended with petrodiesel, as it sustains the green house phenomenon by reducing the impact of CO₂ emission from motor engines [1,2]. Its consumption is approximately 80% of the whole biofuels in Europe [3]. Biodiesel is mainly composed of fatty acids methyl esters (FAME), which are obtained either by transesterification of lipid feedstocks (triglycerides) or direct esterification of fatty acids with short chain alcohol (methanol or ethanol) [4].

Glycerol by-production from biodiesel production process (10 kg of glycerol for each 100 kg of biodiesel) represents the challenge that affects the process economy. Thus, it is imperative that this aggravating glycerol be converted to higher value chemicals; otherwise the economic feasibility of biodiesel is jeopardized. In literature, the transference of this polyol into precious products has been reported [5]. Glycerol can be converted to various chemicals through numerous routes such as etherification [6], hydrogenolysis [7], oxidation [8], transesterification [9]

and dehydration [10]. Besides, glycerol can be esterified with acetic acid to obtain value added products of mono-, di- and triacetyl glycerol (named as MAG, DAG and TAG, respectively), which have found versatile industrial applications [11]. MAG and DAG have applications in cosmetics, medicines and as a starting monomer for the production of biodegradable polyesters [1,11]; whereas TAG has salutary application as a fuel/biodiesel additive [12]. Serious attentions have been devoted on studying glycerol esterification with acetic acid using different solid acid catalysts [1,11,13–16].

Traditionally, glycerol esterification with acetic acid is performed over conventional acids as homogeneous catalysts [11]. Although, the main disadvantage of using such catalysts comprises the effluent acid disposal, leads to serious environmental and technical problems. Therefore, employing heterogeneous acid catalysts can contribute to overcome these drawbacks. Due to their stronger Brønsted acidity than conventional solid acids like mixed oxides and zeolites, Keggin type heteropolyacids (HPAs) can be employed instead of classical homogeneous acids for both acid and redox catalysis [17]. Some drawbacks of bulk HPAs like low thermal stability, high solubility in water and polar media and low surface area (1–10 m² g^{−1}) can be improved by functionalizing them into the framework of high surface area porous supports (silica, activated carbon, zirconia, polymers and acidic ion-exchange resin) [11,18,19]. In addition, the number of accessible acid sites and the

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