Catalytic upgrading of renewable levulinic acid to ethyl levulinate biodiesel using dodecatungstophosphoric acid supported on desilicated H-ZSM-5 as catalyst

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ABSTRACT

Levulinic acid (LA) is considered as a renewable platform chemical and can be used for the synthesis of variety of important fuels and chemicals. In particular, its esterification with ethanol produces ethyl levulinate (EL) would be green process, as it can be used as diesel miscible biofuel (DMB), preventing global warming by decreasing atmospheric CO_2.

This study explores the use of modified H-ZSM-5 by desilication viz.; DH-ZSM-5 and dodecatungstophosphoric acid (DTPA) loaded on DH-ZSM-5 for esterification of LA with ethanol aiming to EL. Different degree of desilication of H-ZSM-5 was performed by using aq. NaOH (0.2–1.5 M) at 338 K for 30 min and then DTPA was loaded on these desilicated H-ZSM-5 (DH-ZSM-5) support. H-ZSM-5, DH-ZSM-5 and DTPA on these DH-ZSM-5 samples were characterized by powder X-ray diffraction (XRD), N_2 adsorption–desorption, pyridine chemisorbed IR spectroscopy, Temperature Programmed Ammonia Desorption (TPAD). The increase in conversion of levulinic acid was observed from 28% to 94% with increase of DTPA loading from 0% to 15%. The increased LA conversion may be due to increase in total acidity from 43.14% to 84.31%.

The use of DH-ZSM-5 as support for deposition of DTPA may be reported for the first time. The present work also extended to optimize process parameters such as DTPA loading on DH-ZSM-5, catalyst to LA ratio, LA to ethanol molar ratio, speed of agitation, particle size reaction temperature and catalyst reusability. Kinetic study based on pseudo-homogeneous (P-H) model is also presented. The experimental results follow second order kinetics.

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1. Introduction

The inevitable depletion of petroleum resources, tempted to devote more effort to replace the fossil resources with renewable feedstock such as biomass for achieving a sustainable future. In this context, several bio-based renewable platform chemicals and various synthesis routes on these chemicals have been proposed [1–5]. Among these routes, the synthesis of levulinate esters from levulinic acid (LA) has been attracting especial attentions because LA is one of the top biomass derived platform molecule that can be made from C_6 sugar carbohydrates derived from renewable lingo-cellulose [6]. Levulinate such as ethyl, methyl, and *n*-butyl levulinate are obtained by esterification of levulinic acid (LA). These

levulinates or esters are having various potential applications in flavoring and fragrance industry [7]. Moreover, ethyl levulinate (EL) can be used up to 5 wt.% as the diesel miscible biofuel (DMB). Addition of EL to the diesel leads to modification in the fuel properties such as a clean burning fuel with high lubricity, stability in flashpoint, reduction in sulfur content, improvement in viscosity [5,7–10].

Traditionally EL was synthesized by using homogeneous catalysts such as HCl, H_3PO_4 and H_2SO_4 [11–14]. These inorganic liquid acids cause environmental problems in disposal, containment, handling and cannot be regenerated due to their toxic and corrosive nature. Very recently, this reaction has regained interest of many researchers and has been re-examined extensively with more robust and industrially benign greener catalysts, i.e., recyclable strong solid acids to replace and overcome the drawbacks of above conventional liquid acid catalysts.

For this purpose, eco-friendly solid acid catalysts including sulfonic acid functionalized (i.e., SO_3H-SBA-15, sulfated zirconia

and beta, Y, ZSM-5 and mordenite zeolite) [15], silica-supported heteropolyacids (HPA/SiO$_2$) [9], montmorillonite-supported heteropolyacids (HPA/K10) [16], sulfated metal oxides (i.e., SO$_4{}^{2-}$/TiO$_2$ and SO$_4{}^{2-}$/ZrO$_2$) [17,18] and a commercial sulfonic resin (Amberlyst-15) [8] were used in this process.

It is still a challenge to develop a robust, stable and environmentally benign solid acid catalyst that can improve the efficiency of EL synthesis.

Heteropolyacids (HPAs) are an interesting class of well-defined super strong solid Brönsted acids, exhibiting excellent catalytic behaviors in a wide variety of acid catalyzed reactions [19,20]. The disadvantages of HPAs including small specific surface area and high solubility in polar media can be overcome by dispersing them within porous supports. Recently, HPAs such as H$_6$P$_2$W$_{18}$O$_{62}$/SiO$_2$ [9] and H$_3$PW$_{12}$O$_{40}$/K10 [16] have been employed for synthesis of ethyl and n-butyl levulinate respectively. However, their catalytic activity is mostly depends on higher loading of H$_6$P$_2$W$_{18}$O$_{62}$ or H$_3$PW$_{12}$O$_{40}$. Amongst all reported HPA's dodecatungstophosphoric acid (DTPA) is the most stable, having highest Brönsted acidity, less volatile, less corrosive, high thermal stability up to 573–623 K [19,21–25].

H-ZSM-5 (zeolite) is used in various catalytic applications due to the unique combination of properties such as hydrothermal stability, well-defined micro-porosity and acidity; however, their catalytic applicability is restricted due to diffusional limitations for bulk molecules. The diffusional constrains can be minimized by a controlled formation of intra-crystalline meso-pore system. Recently, the controlled extraction of framework silicon in alkaline medium, referred to as desilication post-treatment, has resulted in a promising, efficient methodology to produce extended mesoporosity in H-ZSM-5 [26–30]. This combination of use of DTPA on desilicated H-ZSM-5 can be an efficient robust catalyst for EL synthesis.

Based on available literatures, this probably may be the first report on use of DTPA supported on desilicated H-ZSM-5 for the synthesis of EL by esterification of renewable levulinic acid with ethanol as an alkylating agent. The effect of degree of desilication on LA conversion was investigated. The present work also extended to optimize process parameters such as DTPA loading on DH-ZSM-5$_{97}$, percent catalyst loading, LA to ethanol molar ratio, reaction temperature and catalyst reusability. Second order pseudo-homogeneous (P-H) kinetic model is proposed.

2. Experimental

2.1. Chemicals and reagents

Dodecatungstophosphoric acid [H$_3$PO$_4$·12WO$_3$·xH$_2$O] (DTPA) was obtained from M/s S.d. Fine Chem. Ltd., Mumbai (India). Levulinic acid (99%) and ethanol (99%) were obtained from M/s E. Merck, Mumbai (India). All the reagents were of analytical grade and used without further purification.

2.2. Catalyst preparation and catalytic evaluation

H-ZSM-5 with Si/Al ratio 37 was synthesized as per the reported procedure [31]. The H-ZSM-5 was modified by desilication with 0.2, 1.0 and 1.5 M aq. NaOH at 338 K for 30 min. For each case 300 ml, aq. NaOH was mixed with 10 g of H-ZSM-5 in a flask and kept at 338 K for 30 min. After modification, the zeolite samples were transformed into ammonium forms by threefold ion exchange with aq. 0.1 M ammonium nitrate (in the proportion 10 ml g^{-1} of desilicated product for 5 h) without calcination in between ion-exchange procedures. Finally, samples were transformed into the hydrogen forms by calcination in air at 823 K for 5 h.

DTPA on desilicated H-ZSM-5 support was prepared by incipient wetness technique. Typically, for 20 g scale catalyst preparation, the following procedure was adopted: 20 g of support, viz., DH-ZSM-5$_{97}$, was taken. A 2.0 g amount of DTPA was weighted, which corresponds to 10% (w/w) DTPA loading with respect to DH-ZSM-5$_{97}$ weight. The measured DTPA was dissolved in methanol, which formed a homogeneous solution. The methanolic DTPA solution was added slowly on the measured quantity of DH-ZSM-5$_{97}$ with constant stirring using a glass rod. Initially, the support (DH-ZSM-5$_{97}$) was in a powdered form, but, upon subsequent addition of methanolic DTPA solution, it formed a paste or wet cake. The cake was dried on a water bath at 363 K for 2 h. The sample was further dried in an oven at 393 K for 1 h, in order to achieve complete removal of methanol and the dried catalyst was stored in a sealed bottle. Prior to use, the catalyst sample was dried in an oven at 393 K for 1 h. A similar procedure was used to prepare other compositions of the catalyst up to 25% (w/w) DTPA/DH-ZSM-5$_{97}$.

The synthesized catalyst were evaluated in esterification reaction of levulinic acid with ethanol, which was carried out in a two-necked glass round bottom flask of 100 ml capacity equipped with a reflux condenser to prevent the escape of ethanol, a thermometer and a magnetic stirrer. The temperature was maintained within an accuracy of ±0.5 K by an electric-heated thermostatic oil bath. The flask was charged with levulinic acid and the ethanol, both weighted sequentially, followed by the addition of the catalyst. The reactant amounts were calculated according to the desired molar ratio for each reactant (ethanol: LA). Then, the system was heated up to desired temperature (349–357 K), the reaction was carried out for 4–6 h and finally the product was collected after removing the catalyst.

The liquid reaction products were analyzed by using gas chromatography (GC-1000) (packed column, liquid phase 5% SE-30, solid support CHW-HP, 1/8′ diameter × 8′ length) with nitrogen as a carrier gas and programmable temperature range of 313–473 K. The reaction products were also confirmed by GC–MS (Shimadzu-QP 5000).

2.3. Catalyst characterization

The catalyst samples were characterized by using various techniques. The phase identification, degree of crystallinity and purity were determined by powder X-ray diffraction (XRD). The XRD patterns were recorded on X-ray diffractometer (P Analytical PXRD system, Model X-Pert PRO-1712) using Cu Kα radiation at a scanning rate of 0.0671 s^{-1} in the 2θ ranging from 5° to 50°. The degree of crystallinity of disilicated sample is estimated by taking the ratio of summation of integrated peak areas of the peaks appearing at 2θ = 22.5–25° of the test sample to the summation of the integrated peak area of the same peaks in the parent sample.

Low temperature (77 K) nitrogen adsorption and desorption isotherms were obtained using SA 3100 analyzer (Beckman Coulter, CA, USA). The calcined sample was degassed at 573 K for 10 h prior to measurements. The specific surface area is calculated using Brunaer–Emmett–Teller (BET) method.

The nature of acid sites (Brönsted and/or Lewis) in the catalyst was elucidated by ex situ pyridine-FTIR. The catalyst powder sample was activated at 673 K for 2 h, followed by cooling to room temperature under high vacuum. It was then exposed to pyridine vapors for 2 h. The physi-sorbed pyridine was driven off by activating at 423 K for 2 h under high vacuum. The FTIR spectra were recorded on a Shimadzu (Model-820 PC) spectrophotometer under DRIFT (Diffuse Reflectance Infrared Fourier Transform) mode.

The overall acidity was measured by Temperature Programmed Ammonia Desorption (TPAD) using a Micromeritics AutoChem (2910, USA) equipped with thermal conductivity detector. Prior to the measurements, sample was dehydrated at 773 K in He