Journal of Industrial and Engineering Chemistry xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

KCC-1/Pr-SO_3H as an efficient heterogeneous catalyst for production of *n*-butyl levulinate from furfuryl alcohol

Zahra Mohammadbagheri[a], Alirza Najafi Chermahini[b,*]

[a] Chemistry Group, Pardis College, Isfahan University of Technology, Isfahan 84156-83111, Iran
[b] Department of Chemistry, Isfahan University of Technology, 84154-83111 Isfahan, Iran

ARTICLE INFO

Article history:
Received 17 June 2017
Received in revised form 9 December 2017
Accepted 16 January 2018
Available online xxx

Keywords:
n-Butyl levulinate
Furfuryl alcohol
Biomass conversion
KCC-1
Solid acid catalyst

ABSTRACT

In this study, production of *n*-butyl levulinate from furfuryl alcohol was investigated using KCC-1/Pr-SO_3H as an efficient heterogeneous catalyst. The catalyst was prepared and characterized using FT-IR, N_2 adsorption/desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), pyridine-adsorbed FT-IR spectroscopy and TGA techniques. The effects of different parameters on the reaction conditions including temperature, reaction time, catalyst amount, and furfuryl alcohol volume were evaluated. The highest yield of *n*-butyl levulinate was 81.9% at 120 °C after 3 h. The catalyst was recovered and reused at least four times with insignificant change in yield of *n*-butyl levulinate.

Introduction

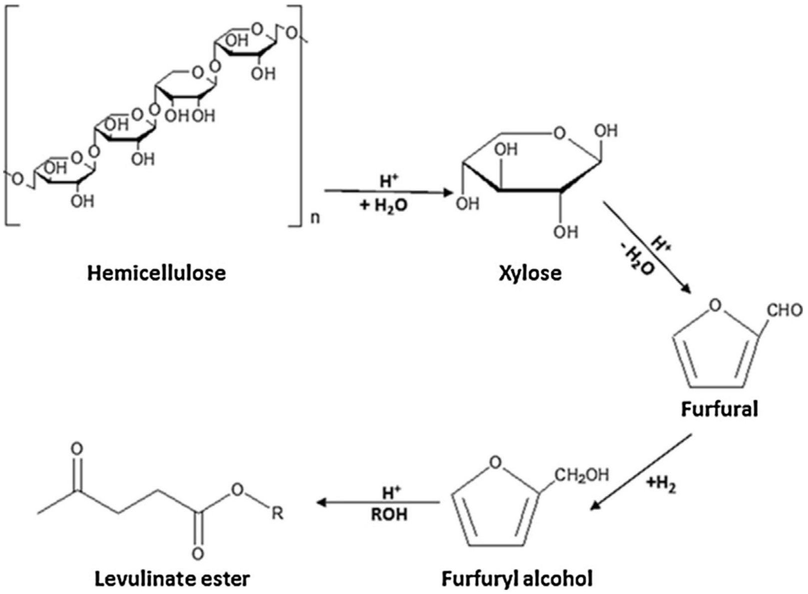
Fossil fuel resources are the major source of energy in the world, but with the drastic consumption of these non-renewable resources and the resulting global warming caused by the emission of greenhouse gases, scientists are thinking about using alternative resources such as wind, biomass, solar, geothermal and hydroelectric to supply world's energy needs. Among these new resources of energy, biomass is considered as a possible substitute for the fossil fuels because this renewable resource is low-cost, available and abundant to produce fuels and different chemicals [1–8]. Levulinate esters are one of the most important compounds derived from biomass due to its wide range of applications in the flavoring and fragrance industry. In addition, they also have excellent properties that make them suitable for use as diesel fuels [9–12]. Levulinate esters can be synthesized from the pentoses, mainly xylose, in hemicelluloses (Scheme 1). In this process, furfural is produced from acid hydrolysis and dehydration of pentose, then the hydrogenation of furfural leads to formation of furfuryl alcohol which can be converted to levulinate esters by acid catalyzed reaction in alcohol media [13,14]. The alcoholysis step of this approach is carried out in the presence of homogenous acid catalysts such as H_2SO_4 and HCl, but the use of heterogeneous catalysts instead of these mineral acids is more advantageous because they are no corrosive, separable, recyclable and environmentally friendly [15–17]. Recently, various heterogeneous solid acid catalysts were tested for the synthesis of alkyl levulinate from furfuryl alcohol alcoholysis. For instance, Zhang et al. studied the conversion of furfuryl alcohol into *n*-butyl levulinate using solid catalyst methylimidazolebutylsulfate phosphotungstate ($[MIMBS]_3PW_{12}O_{40}$). The object product was synthesized with a yield up to 93% at 110 °C after 12 h, but catalyst reusability was not reported [18]. Neves et al. used an aluminosilicate Al-TUD-1 catalyst for the production of ethyl levulinate from furfuryl alcohol and achieved a high ethyl levulinate yield of 80% at 140 °C after 24 h. This catalyst was reused for three times without any change in the product yield [19]. In another study, He and co-workers produced ethyl levulinate from the alcoholysis of furfuryl alcohol using ZrAl-mp as a catalyst. A high ethyl levulinate yield of 80% was achieved at 140 °C after 24 h, but it decreased to 21% after three cycles [20]. Cara et al. investigated the catalytic activity of propylsulfonic acid-functionalized mesoporous silica (SBA-15-SO_3H) in the reaction of furfuryl alcohol with *n*-butanol. The yield of *n*-butyl levulinate was 96% at 110 °C after 4 h. However, the reuse of the catalyst was not assayed [21]. Zhao et al. synthesized ethyl levulinate from the reaction of furfuryl alcohol and ethanol in the presence of SO_4^{-2}/TiO_2 catalyst. This catalyst showed good activity at 125 °C after 2 h reaction time, but the ethyl levulinate yield decreased from 74.6% to 47.8% after three consecutive runs [22]. Srinivasa et al. reported synthesis of ethyl levulinate using titanium modified heteropoly

---

[*] Corresponding author at: Department of Chemistry, Isfahan University of Technology, 84154-83111 Isfahan, Iran.
E-mail addresses: anajafi@cc.iut.ac.ir, najafy@gmail.com (A. Najafi Chermahini).

https://doi.org/10.1016/j.jiec.2018.01.020
1226-086X/

Please cite this article in press as: Z. Mohammadbagheri, A. Najafi Chermahini, KCC-1/Pr-SO_3H as an efficient heterogeneous catalyst for production of *n*-butyl levulinate from furfuryl alcohol, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.01.020



Scheme 1. Levulinate ester production from hemicellulose.

tungstate catalyst. The yield of ethyl levulinate was 98% at 120 °C after 30 min [23]. Huang et al. investigated the catalytic activity of various metal salts in the reaction of furfuryl alcohol and methanol. Among these catalysts, $Al_2(SO_4)_3$ displayed the best performance and methyl levulinate was synthesized with a yield of 80.6% at 150 °C after 5 min. The catalyst was also reused six times without considerable decrease in the activity [24]. Enumula et al. synthesized a series of Al_2O_3/SBA-15 catalysts with various weight percentages. The alcoholysis of furfuryl alcohol with *n*-butanol using 20 wt % Al_2O_3/SBA-15 yielded 94% selectivity to *n*-butyl levulinate with complete conversion of furfuryl alcohol at 110 °C [25]. However, most of these catalysts have some problems such as intricate recycling, complicated preparations, and high cost. In this context, fibrous nanosilica (KCC-1/Pr-SO_3H) was used as a new heterogeneous catalyst for the production of *n*-butyl levulinate from furfuryl alcohol in *n*-butanol. In this case, KCC-1 was selected as an efficient silica support with easily accessible high surface area and good physical and textural properties [26,27]. For this purpose, KCC-1 was prepared and grafted with propylsulfonic acid groups to increase catalyst acidity. Then the performance of this catalyst was investigated for synthesis of *n*-butyl levulinate. The optimum reaction conditions and catalyst reuse were also examined.

Experimental

Materials

Cetyltrimethylammonium bromide (CTAB, >99%), urea and tetraethyl orthosilicate (TEOS, >98%) were obtained from Dae-Jung, S. Korea. Cyclohexane, toluene, 1-pentanol, *n*-butanol, and furfuryl alcohol (98%) were obtained from Merck. (3-Mercaptopropyl) trimethoxysilane and *n*-butyl levulinate were obtained from Aldrich.

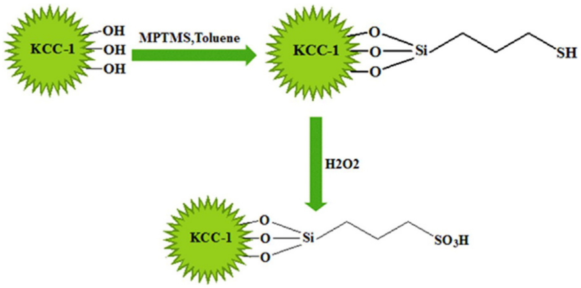
Catalyst synthesis

Synthesis of KCC-1

Fibrous silica KCC-1 was synthesized according to a pervious procedure reported elsewhere [28]. Briefly, 1 g CTAB was dissolved in 10 mL deionized (DI) water followed by addition of 0.6 g urea. This solution was stirred for 3 h and added to a solution of 2.5 g TEOS, 30 mL cyclohexane and 1.5 mL pentanol. After 30 min continuous stirring at room temperature, this solution was refluxed at 120 °C under stirring for 4 h and placed in an oven at 80 °C for 24 h. The mixture was cooled to room temperature and centrifuged (3 min, 6000 rpm) to separate the formed silica particles. These particles were washed with distilled water (three times) and acetone (two times) and then dried for 24 h in oven. Finally, the sample was calcined in air at 550 °C in electrical furnace for six hours to remove directing agent.

Preparation of KCC-1/Pr-SO_3H catalyst

In order to functionalize KCC-1 with propyl sulfonic acid groups through post-grafting, 1.5 g of synthesized KCC-1 material was added to a flask containing 40 mL anhydrous toluene and 2 mL mercaptopropyltrimethoxysilane and the mixture was refluxed for 24 h. After cooling to room temperature, the solution was filtered, and the solid KCC-1/Pr-SH was washed with ethanol using a Soxhlet extractor and dried at 80 °C overnight. Then, obtained KCC-1/Pr-SH was added to 25 mL of 35% H_2O_2 by continuous stirring at room temperature for 24 h, washed with methanol repeatedly, and dried at room temperature to yield KCC-1/Pr-SO_3H [28]. According to elemental analysis, 0.2675 mmol g^{-1} of sulfonic acid group was grafted to the surface of the KCC-1/Pr-SO_3H sample. The synthetic process for KCC-1/Pr-SO_3H is depicted in (Scheme 2).



Scheme 2. Synthesis of KCC-1/Pr-SO_3H solid acid catalyst.

Please cite this article in press as: Z. Mohammadbagheri, A. Najafi Chermahini, KCC-1/Pr-SO_3H as an efficient heterogeneous catalyst for production of *n*-butyl levulinate from furfuryl alcohol, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.01.020