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Catalytic upgrading of furfuryl alcohol to alkyl levulinates under batch microwave irradiation

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PURPOSE OF THE ABSTRACT
Alkyl levulinates (ALs), which have been identified as one of top ten biorefinery candidates, are a kind of promising renewable fuel additives and platform chemicals for the synthesis of angelica lactone, GVL, valerates, as well as good building blocks.1 Generally, ALs were produced by direct esterification of levulinic acid over acidic catalysts or enzymatic methods,2,3 however, in the production of levulinic acid, its separation and purification are costly, which made it unsuitable for as the raw material for this purpose.4 Recently, great efforts were devoted to develop new methods to produce ALs from various feedstock, such as raw biomass,5 carbohydrates,6 5-hydroxymethyl furfural or furfural,7 and furfuryl alcohol.8 Among them, furfuryl alcohol is a promising starting material due to its easy accessibility from furfural by reduction of its aldehyde function. Besides, each year around 62 % of furfural was used for furfuryl alcohol production, and it has been oversupplied in the chemical market.9 Thus, the development of a feasible and competitive pathway for furfuryl alcohol upgrading into ALs is strongly demanded. Various homogeneous and heterogeneous catalysts have been concretely investigated in recent years. However, several defects of these above-mentioned catalysts, such as the complex preparation process, the cost, environment concerns, limited their applications to some extent. Regarding the fact that microwave heating could improve the reaction rate of furfuryl alcohol methanolysis to methyl levulinate six (6) times when compared to conventional heating method.10

The present study firstly showed a cheap and commercially available activated carbon (AC) as an efficient catalyst for the alcoholysis of furfuryl alcohol (FA) to alkyl levulinates under batch microwave radiation. The catalyst gave an impressive methyl levulinate (ML) yield of 78 % in only 5 min at 170 oC in the presence of 3 mL 0.2 M FA and 100 mg AC. Various reaction parameters in dependence of time such as temperature, catalyst and feedstock loadings as well as solvent types have been optimized. The re-utilization experiments of the catalyst showed that the activity related to the acidic groups of the catalysts, and the deactivation was due to the leaching of acidic species of sulphur, which was easily extracted by the solvent. Notably that extremely low concentration of the active species extracted from AC (less than 1 wt %) could also give ML in 62 % yield. The present study provided a promising way for ALs synthesis over cheap, commercially available and environmentally benign catalyst.

FIGURES

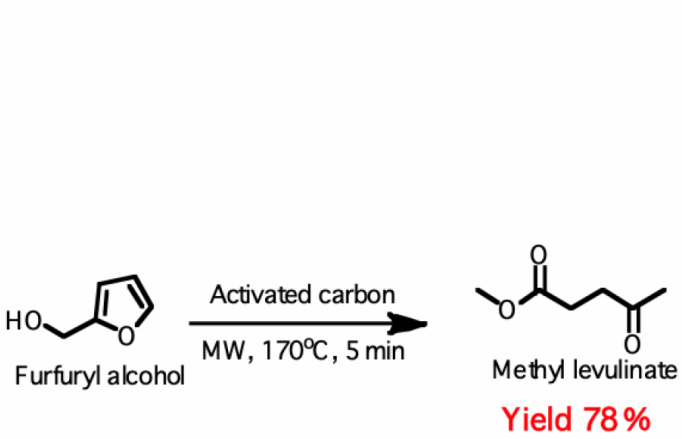

FIGURE 1

Batch microwave-assisted synthesis of methyl levulinate

Batch microwave-assisted synthesis of methyl levulinate

FIGURE 2

KEYWORDS

heterogeneous catalysis | biomass | microwave | methyl levulinate

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