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Sustainable Valorization of Cellulosic Biomass-Derived ?-Valerolactone to ?-Methylene-?-Valerolactone over Hierarchical Superior Basic Zeolite via Tandem Flow Process

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PURPOSE OF THE ABSTRACT

The necessity for production eco-friendly fine chemicals and polymers motivate researchers for a transition towards renewable and sustainable resources [1-3]. Particularly, cellulosic biomass, i.e., cellulose and hemicellulose, was successfully and efficiently valorized towards large amount of green building blocks such as levulinic acid (LA), ?-valerolactone (GVL) and 5-hydorxymethylfuran (HMF) [4]. Of these, GVL which easily form in large quantity from hydrodeoxygenation of cellulosic biomass, exhibits an excellent solvent properties and it is a main precursor for synthesis of high value fine chemicals and polymers e.g., valeric acid and ?-methylene-?-valerolactone (MeGVL) [1]. In this regards, MeGVL is an acrylic monomer with similar structure and properties to methyl methacrylate (MMA) [1-2]. This similarity gives MeGVL the potential for an eco-friendly large scale production of poly(?-methylene-?-valerolactone) (PMeGVL), which could substitute the fossil-based poly(methyl methacrylate) (PMMA). However, MeGVL can be synthesized from GVL by basically catalyzed ?-methylenation reaction using formaldehyde (FA) as methylene source.

Herein and for the first time, we present a unique tandem flow process for MeGVL synthesis from GVL over superior basic hierarchical zeolite in the present of trioxane as FA source (scheme 1). Furthermore, polymerization of derived-MeGVL was performed via visible light induced green polymerization approach over g-CN as heterogeneous metal-free catalyst.

For this purpose, 5 wt.-% Cs catalysts supported hierarchical Beta zeolite (H-Beta) with different Si/Al ratio , i.e., 150, 220 and 300, were prepared via incipient wetness impregnation. Over all tested catalyst, similar GVL conversion profiles were observed by utilizing different reaction temperatures, i.e., 553 K, 568 K and 583 K (Fig. 1). However, at 568 K the selectivity towards MeGVL was found to be the highest, i.e., ~55%, over 5Cs/H-Beta150 (Fig. 1). In additiona to MeGVL, 4-pentenoic acid and methyl 4-pentenoate were observed as by-products with overall yield up to 15%. The high selectivity of MeGVL using H-Beta150-based catalyst is due to the high specific mesopores surface area (398 m2 g-1) with respect to other catalyst. Furthermore, CO2-TPD proven that H-Beta150-based catalyst possesses a mild basicity, whereas H-Beta220 and 300 exhibit a strong basic sites which is give instability in aldol condensation due to its fouling.

Finally, Polymer formation from the reaction mixture at 568 K was confirmed with 1H-NMR (maybe some small comment), and SEC (?: 1.92, Mn: 4200 g/mol).

In conclusion, for the first time we have successfully synthesized green monomer, i.e., MeGVL, with high yield (~55%) from GVL in the presence of trioxane as formaldehyde source by utilizing superior basic zeolite in flow system. These findings envisaged to pave the way for a sustainable eco-frindly polymer production from

renewable resources.

[1] D. Esposito, M. Antonietti, Chem Soc Rev, 44 (2015) 5821.
[2] N. Brun, P. Hesemann, D. Esposito, Chem Sci, 8 (2017) 4724.
[3] P.C. Bruijnincx, B.M. Weckhuysen, Angew Chem Int Ed, 52 (2013) 11980.
[4] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411.

FIGURES

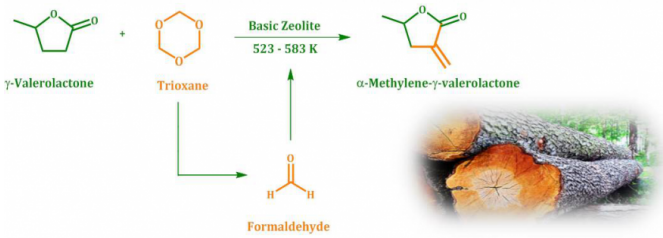

FIGURE 1

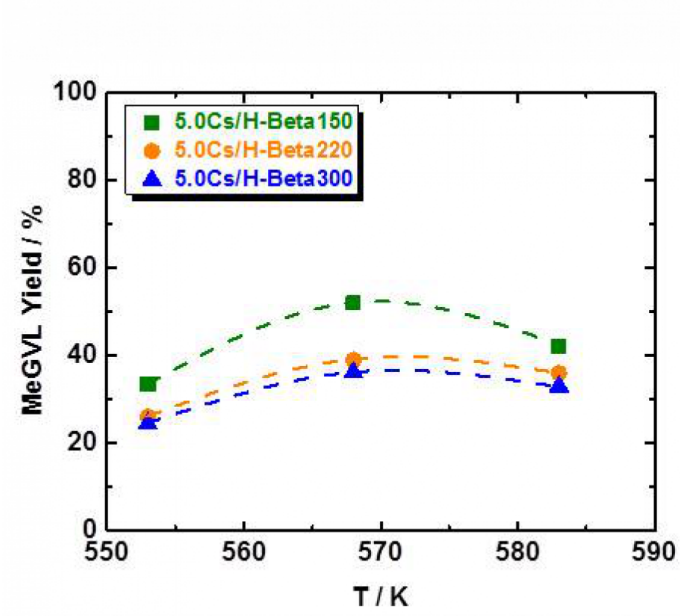

FIGURE 2

Fig. 1

MeGVL yield (right) as function of reaction temperature over 5.0 wt.-% Cs catalyst supported on 3 different hierarchical Beta zeolite (H-Beta), i.e., Beta150, Beta220 and Beta300 in GVL upgrading to MeGVL using trioxane as a formaldehyde source; reaction

KEYWORDS

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[2] N. Brun, P. Hesemann, D. Esposito, Chem Sci, 8 (2017) 4724.
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[4] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411