Promotional Role of Water for Steering the Product Selectivity in Levulinic Acid Hydrogenation

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Abstract: Both alkyl esters and γ-valerolactone (GVL) derived from levulinic acid (LA) are of vital importance in biomass valorisation. After screening several metals and supports, we found that La_2O_3 supported cobalt catalyst was very efficient for a cascade LA hydrogenation to GVL via esterification. LA hydrogenation in methanol alone yielded methyl levulinate (MeLA) as a major product along with 43% of GVL. Interestingly, hydrogenation in water gave almost complete selectivity to GVL nevertheless; it was associated with significant metal leaching. Suppression of metal leaching and enhancement in selectivity to GVL could be achieved by methanol: water solvent system. 20% Co/La_2O_3 catalyst was characterized by XRD, XPS, HR-TEM, CO_2-TPD and NH3-TPD

Keywords: Levulinic acid, Co/La_2O_3, water.

1. Introduction

Lignocellulose is one of the important sustainable resources for producing an array of products having applications in energy as well as commodity and fine chemical sectors. Carbohydrate polymers such as cellulose, hemicelluloses on hydrolysis give various primary platform molecules from which value added chemicals can be obtained by developing multifunctional catalysts and process strategies[1-2]. Levulinic acid (LA) is one such most important platform molecule which on hydrogenation gives various industrially important products like γ–valerolactone (GVL), alkyl levulinate, 1, 4-pentanediol (PeDO), 2-methyl tetrahydrofuran (MeTHF), pentatonic acid and its ester etc. Among these, GVL is of seminal interest being used as fuel additive, solvent, liquid fuel, and also is an ideal precursor for the production of several valuable chemicals[3-4].

2. Experimental

Cobalt catalysts were prepared by incipient wet impregnation from cobalt nitrate (Thomas beaker) and lanthanum oxide prepared by co-precipitation method from lanthanum chloride. In a typical procedure, 20% weight of cobalt nitrate hexahydrate (Thomas beaker) dissolved in 80-90mL water under stirring, followed by the slow addition of prepared La_2O_3 support in a solution after complete dissolution of metal precursor in water. The solution was kept for stirring for 2 h at room temperature. After 2hrs catalyst was reduced with sodium borohydride, kept it for 30 min under stirring. Then filter the catalyst and wash with water till pH becomes neutral. Catalyst was dried at 120 ^{0} C for 8-10 h. Prepared catalyst named as 20% Co/La_2O_3.

Reactions were performed in a 300 mL stainless steel autoclave equipped with overhead stirrer, a pressure gauge and automatic temperature control facility with charging of 5 g levulinic acid, 100 mL (MeOH) solvent and 0.5 g catalyst and reactor was pressurized with H_2 to 500psi, temperature maintained at 200°C for 5h. The desired temperature of reaction mixture was maintained by heating mantle. After completion of reaction, chilled water was passed through the internal cooling coil of reactor to bring the temperature and pressure down to ambient conditions, the remaining pressure was released and the reaction mixture was filter to separate the solid catalyst and the product solution. Initial and final reaction mixture was analyzed by using GC equipped with FFAP capillary column and Flame Ionization Detector.

3. Results and discussion

In present work cobalt catalysts were studied for levulinic acid hydrogenation to achieve maximum yield of GVL using methanol water mix solvent system. Initially, Levulinic acid hydrogenation reaction was carried out using 20% Co/La_2O_3 catalyst in MeOH, LA first convert into its methyl ester (MeLA) which further hydrogenated to give GVL with 43% selectivity along with pentanoic acid and remaining MeLA. Therefore water is added to the reaction mixture to manipulate the selectivity of MeLA, GVL and PA. Interestingly, water promotes the hydrogenation reaction of methyl levulinate to GVL; thus selectivity of GVL was increased up to 75%.

Table 1. Solvent effect on Levulinic acid hydrogenation

Sr.No.	Catalyst	Solvent	Conv, %	Selectivity, %		
				GVL	MeLA	PA
1	20% Co/La_2O_3	MeOH	99	43	48	9
2	20% Co/La_2O_3	MeOH:H_2O	99	75	19	6

Reaction conditions: Levulinic acid, 5g; solvent,100ml; catalyst, 0.5g; temperature, 200^{0}C; H_2 pressure, 500 psi; reaction time, 5 h.

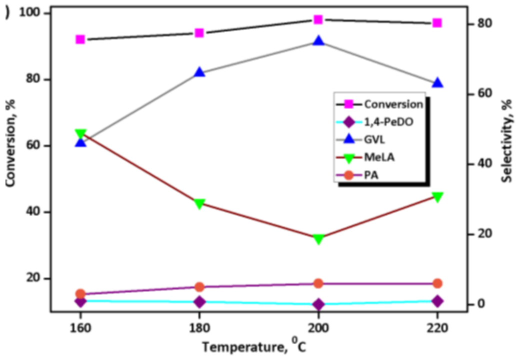

Figure 1. Effect of temperature.

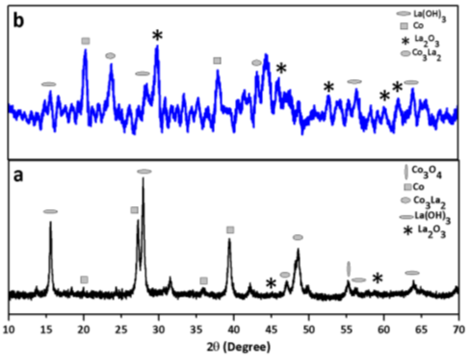

Figure 2. XRD of fresh(a) and used(b) catalyst.

4. Conclusions

Co supported on various supports were prepared and screened for levulinic acid hydrogenation in organic and aqueous medium. Among these, Co/La_2O_3 gave equal selectivities to MeLA and GVL in methanol medium. GVL selectivity over Co/La_2O_3 could be enhanced in aqueous methanol as the release of hydrogen form $La(OH)_3$ species and hydrogen bonding present on catalyst surface becomes more facile required for hydrogenation of MeLA. Both XRD and XPS confirmed the presence of oxide, hydroxide and Co-La species in the catalyst sample. However, used catalyst exhibited significant increase in oxide peak intensity while corresponding decrease in hydroxide peak intensity confirming the role of support in LA hydrogenation. This structural change during reaction offered higher exposure of the active sites resulting into the higher selectivity to GVL in aqueous medium. The catalyst showed consistent performance for four uses while marginal decrease in GVL selectivity with higher extent of MeLA formation. This work demonstrates the efficient non-noble metal catalyst integrated with optimized reaction conditions to tailor the ester and GVL selectivities in LA hydrogenation.

References

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