

Rhodium porphyrin molecule-based catalysts for the hydrogenation of biomass derived levulinic acid to biofuel additive γ -valerolactone

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Rhodium-*meso*-tetraphenylporphyrin (RhTPP) and rhodium-*meso*-tetrakis(4-carboxyphenyl)porphyrin (RhTCPP) complexes were synthesized and surface grafted on amine-functional mesoporous molecular sieves. The formation of ligands (TPP and TCPP) and its rhodium complexes (RhTPP and RhTCPP) were evident with the help of ¹H NMR, ¹³C NMR, mass spectral and elemental (CHN) analysis. The absence of pyrrole proton of the porphyrin units on RhTPP and RhTCPP confirmed the successful formation of metallo-macro-molecules. Further, RhTPP and RhTCPP were fixed on the surface of SBA-15 through amino-silane as linker. The rhodium containing homogeneous (RhTPP and RhTCPP) and heterogenised catalysts (RhTPP-SBA-AM and RhTCPP-SBA-AM) were used for biomass-derived levulinic acid hydrogenation. Further, the synthesized catalysts were utilized for the hydrogenation of various organic molecules having arene, carbonyl, and alkene functionality under moderate reaction conditions. Both the homogeneous and heterogeneous catalysts showed more than 95 % levulinic acid conversion even after four cycles. The homogeneous RhTPP and RhTCPP yielded γ -valerolactone (GVL) as a major product, whereas the use of heterogeneous catalyst gives only comparable γ -valerolactone (GVL) selectivity, with improved reusability, and recyclability in presence of relatively less rhodium complexes. Among the RhTPP and RhTCPP, the RhTPP shows better selectivity for γ -valerolactone (GVL) compared to RhTCPP. Further, as the number of catalytic run increases, there is a gradual increase in diol selectivity, which is predominant in RhTCPP, possibly due to the presence of hydrophilic carboxylate ion facilitate the interaction of water by-products with γ -valerolactone and favour the diol formation. The hydrophobic environment of RhTPP catalyst facilitates γ -valerolactone as the major product even in the fifth run.

1. Introduction

Hydrogenation of organic molecules is one of the most important process in synthetic organic chemistry. It has wide applications ranging from fine chemicals to pharmaceutical synthesis.¹⁻³ Furthermore, hydrogenation process is very important in petrochemical industries.^{4,5} In general, hydrogenation involves transfer of a dihydrogen molecule to unsaturated moieties in a molecule by using various hydrogenation sources such as gaseous hydrogen, hydrazine and formic acid. Often, catalysts play a major role in improving reactivity, reaction rates and selectivity of hydrogenation process.⁶ Development of ideal and improved catalysts for the hydrogenation processes is one of the most fascinating, but challenging^{7,8} area in this field of research. In industries, the need of hydrogenation process is highly demanding due to the application in the production of fine chemicals such as value-added platform molecules⁹ and low-aromatic fuels.¹⁰ Hydrogenation of organic compounds through green processes for the production of gasoline, fine chemical intermediates and value-added chemicals¹¹ are important processes in the bio-refining industry. On the other hand, depletion of fossil fuel as

well as increase in the demand on energy resource and fine chemicals, there is an essential requirement of substitute and renewable resources.¹²⁻¹⁴ Based on the current scenario of the economic and sustainability aspects, a feedstock based on biomass appears to be much attractive.^{15,16} Biomass¹⁷ is an alternative and promising raw material for the preparation of chemicals and fuels due to its abundance¹⁸ and inexpensive-renewable sources.^{19,20} For example, cellulose is an important biomass feedstock^{21,22} that can be efficiently converted to valuable chemicals, viz., furfuryl derivative (HMF), levulinic acid (LA), 1,4-pentanediol, and γ -valerolactone (GVL).^{23,24} Among these various processes, γ -valerolactone (GVL) produced from LA plays an important part in viable biomass transformation. It has various applications such as a potential fuel additive, fine chemical intermediates, food ingredient, green solvent²⁵ for lacquers, insecticide and adhesive.^{23,26-29} Furthermore, it can be used as an energy carrier^{30,31} and also in the synthesis of carbon-based products.^{23,27,32} Recently, numerous studies and reviews have been devoted to the production of GVL and 1, 4-pentanediol.³³⁻³⁵ The production of GVL and 1,4-pentanediol from LA began as early as the 1930s using various catalysts, such as rhenium (Re) black³⁶, platinum oxide (PtO₂),^{37,38} zirconium (Zr)-based beta zeolites²⁴, Raney nickel^{39,40} and mixed metal-oxides. In most of the cases, better yields of γ -valerolactone was obtained under severe conditions such as high temperature (e.g. 200-700 °C), pressure (e.g.50-200 bars of H₂) and longer reaction times (20-50 h). Often, the formation of polymerized by-products was evident¹⁰ and the catalysts were not reusable. Thus, it is necessary to develop efficient catalysts which are eco-friendly, economically benign, less energy consuming and safe during the process with mild reaction conditions.⁴¹⁻⁴⁴ Noble metals such as rhodium (Rh), ruthenium (Ru), Platinum(Pt), palladium (Pd), iridium (Ir) Rhenium (Re), nickel (Ni) and base

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