Exploring the effect of acid modulators on MIL-101 (Cr) metal-organic framework catalysed olefin-aldehyde condensation; A sustainable approach for the selective synthesis of nopol

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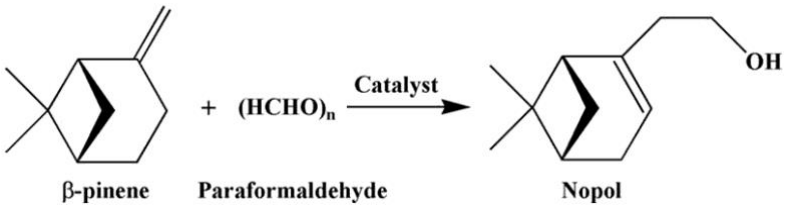
ABSTRACT

The development of efficient and sustainable strategies that evades the utilization of petroleum reserves is highly challenging yet inevitable today. In this context, biomass is a sustainable source of carbon that can be used to minimize the catastrophic effects of fossil resources on the environment [1]. Variety of chemicals, fuels and fuel additives can be obtained from the lignocellulosic biomass [2]. Among them, pine tree derived α and β-pinene have driven the significant research interest for being important bicyclic hydrocarbons from the commercial standpoint [3]. In this regard, the conversion of pine tree derived β-pinene to highly recognized nopol is particularly attractive owing to the widespread applications of nopol (scheme 01).

Scheme 01: Reaction scheme for nopol synthesis by Prins condensation:



Herein, we describe an approach that enables the selective synthesis of nopol with extraordinarily high activity of MIL-101(Cr) catalyst. In particular, the MIL-101(Cr) materials having different textural properties have been synthesized using the three mineralizing agents by hydrothermal method. Four catalysts were characterized by various techniques and tested in the nopol synthesis from β-pinene and PFA condensation. Among the MIL-101(Cr) catalysts screened, the MIL-101(AA) (5 wt.% catalyst concentration) demonstrated the superior catalytic activity for the selective nopol synthesis (figure 01). This remarkable catalytic activity of MIL-101(Cr) is ascribed to its high specific surface area (SSA), accessible active sites in the mesopore architecture and unsaturated Cr^{3+} Lewis acid sites.

We have established a correlation between the superior catalytic performance and textural properties of the materials, which can be tuned by using different mineralizing agents. To realize the unprecedented catalytic activity, the influence of reaction parameters, solvent properties and mineralizing agents have been investigated systematically. To the extent of our knowledge, the catalytic activity of MIL-101(AA) (AA-Acetic acid) is superior to most of the reported materials for this transformation to date. The characterizations of catalytic materials reveal a good correlation between the textural properties and catalytic activity of MIL-101(Cr) catalysts. The MIL-101(AA) catalyst showed consistent results in the recycling experiments (Up to 5 recycles) (figure 02).

Figure 01: Effect of catalyst concentration

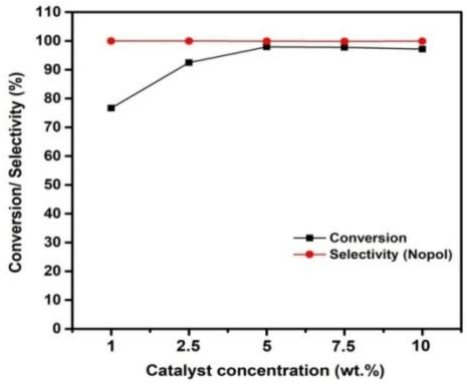
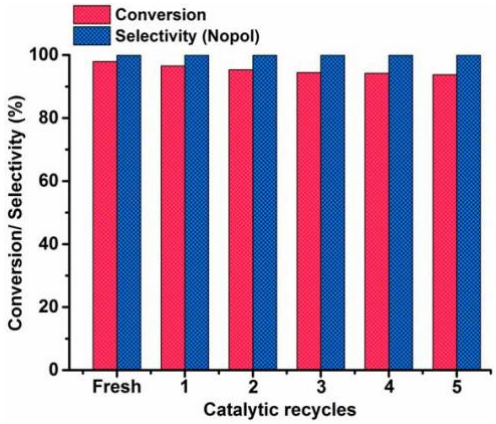


Figure 02: Recyclability studies



Default reaction conditions: Catalyst- MIL-101(AA), catalyst concentration- 5 wt.%, mole ratio- 1:2 (β-pinene: paraformaldehyde), solvent- benzonitrile (5 mL), reaction temperature- 90 °C, reaction time- 6 h, conversions were calculated with respect to limiting reagent (β–pinene).

The results of catalyst recycle and hot filtration experiments have emphasized that the catalyst is resistant towards leaching of active sites and retained its original catalytic activity beyond four recycles. MIL-101(AA) is found to be highly efficient, inexpensive and selective heterogeneous catalyst for the nopol synthesis by β-pinene condensation with paraformaldehyde. This approach opens up new avenues for the efficient conversion of biomass-derived molecules to vale added chemicals.

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