

Catalytic upgradation of biomass-derived phenolic compounds via C-C coupling with small oxygenates

Gul Afreen, Tanmoy Patra, Sreedevi Upadhyayula*

Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi-110016, India

*Corresponding author: sreedevi@chemical.iitd.ac.in

Highlights

- Catalytic activity comparison of different zeolites in *iso*-propylation of *m*-cresol
- Zn-loaded HY zeolite with high Lewis acidity exhibited 87% *m*-cresol conversion
- Maximum catalytic efficiency was obtained at 250 °C and WHSV value of 2.8 h⁻¹
- ZnY selectively produced C-alkylated product thymol (C/O alkylation ratio:32.3)

1. Introduction

With rapid depletion of fossil fuels, the world-wide energy currency has been considered a major industrial concern in last few decades. As a promising prospect, biomass conversion to biofuels and value added chemicals has evolved immensely as alternative renewable energy resources in the last decade.[1] Pyrolysis of biomass results in the formation of bio-oils which are composed of phenolic compounds and small oxygenates, among other compounds. Prior to the high pressure hydroprocessing step, the upgradation of these components to C₁₀-C₁₃ range fuel precursors helps to preserve the carbon fractions by suppressing the gasification of the small oxygenates. Moreover, the reported process is carbon-waste free and also has the potential to produce exclusively fuel range components without any additional industrial waste. In this context, the C-C alkylation reaction between phenolic compounds and small oxygenates like alcohols, obtained as a major components in bio-oils, have become a major industrially important reaction. Furthermore, the obtained alkylated phenolic compounds obtained in this process are used in the paint, rubber, pharmaceutical, and cosmetics industry as fine chemicals.[2]

In the present study, zeolites HZSM5, HBEA, HMCM22, HY, and ZnY were chosen as catalysts, based on their varied acid site densities and pore dimensions, to investigate their overall effect on alkylation of *m*-cresol with *iso*-propanol. The ion-exchange of zinc in zeolites generates the Lewis acid sites by replacing Bronsted acid sites. The objective of this study is to ascertain the effect of the nature and strength of superficial acid sites as well as their pore size on the catalytic activity and product distribution. The acidic property of the zeolites was determined by NH₃-TPD and pyridine-FTIR, and the details of surface and porosity were determined by N₂ sorption.

2. Methods

ZnY zeolite was prepared by ion-exchange method, where HY zeolite was treated with 0.05 M aqueous solution of zinc acetate dehydrate. The solution was then refluxed for 8 h. The obtained mixture was filtered, washed, and dried at 120 °C for 8 h. The above steps were repeated twice to obtain maximum ion-exchange. Finally, the catalyst was calcined at 550 °C for 4 h.[3]

The gas-phase *iso*-propylation reactions of *m*-cresol were carried out in a fixed-bed continuous flow reactor with L/D ratio of ~ 50. The liquid product was analyzed using a NUCON-GC equipped with a CHROMSORB-WHP (2 m × 3.175 mm × 2 mm) column and flame ionization detector (FID).

3. Results and discussion

The effect of different temperatures (200-300 °C) on conversion of *m*-cresol ($X_{m\text{-cresol}}$) and product distribution (S_i) over each catalyst is shown in **Figure 1**. For catalysts HZSM5 and HMCM22, maximum conversion of *m*-cresol was obtained at 225 °C (29% and 31%, respectively). However, for the catalysts HBEA, HY, and ZnY, maximum conversion of *m*-cresol was observed at 250 °C (43%, 70%, and 87%, respectively).

The main products of the reaction were *isopropyl 3-methylphenyl ether* (IPMCE) and mono-*C*-alkylated *m*-cresols (2-*isopropyl-5-methylphenol* (thymol), 4-*isopropyl-3-methylphenol* (4I-3MP), and 3-*isopropyl-5-methylphenol* (3I-5MP)). Di-alkylated *m*-cresols were observed to be the secondary products using these catalysts. Thymol, the desired product, was found to be the most selective product over all the catalysts except HBEA, as it can diffuse at a higher rate than its other isomers through the pore channels of the zeolites owing to smallest effective kinetic diameter (4.57 Å) as well as higher rate of C-C coupling between the adjacent *ortho* carbon of chemisorbed *m*-cresol on the catalyst acidic surface sites through its –OH group and the *iso*-propyl cation.[4]

Among all the catalysts used in this study, ZnY showed highest catalytic activity in terms of conversion of *m*-cresol (87%) at 250°C. This can be attributed to strong Lewis acidity associated with incorporation of Zn²⁺ ions on the silica surface. Thymol was obtained as the major product over ZnY owing to its strong acidic sites which prefer C-alkylation especially at the less hindered *ortho* carbon of aromatic ring of *m*-cresol.

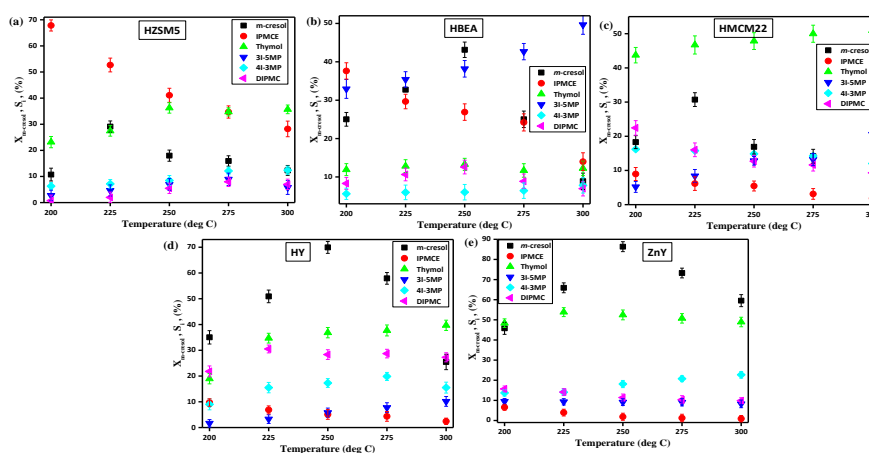


Figure 1. Selectivity (S_i) to products and conversion of *m*-cresol ($X_{m-cresol}$) as a function of temperature for catalysts: (a) HZSM5, (b) HBEA, (c) HMCM22, (d) HY, and (e) ZnY; Reaction conditions: $P_T = 101.3$ kPa, $WHSV = 2.8$ h⁻¹, *iso*-propanol: *m*-cresol molar ratio = 2:1.

4. Conclusions

The catalytic activity study suggested that the conversion of *m*-cresol and selectivity to the alkylated products is strongly controlled by the density, nature, and strength as well as the pore structure of the catalytic active acid sites. ZnY catalyst with highest acid density and strongest Lewis acidity along with wide 3-dimensional pore structures was found to be the best catalyst for the reaction in terms of highest *m*-cresol conversion and exclusive selectivity to the desired product thymol.

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Keywords

Biomass, thymol, *m*-cresol *iso*-propylation, solid acid catalysts