Upgrading of plastic pyrolysis oil model compounds over ZSM5-based catalysts: Effect of reactor type and operating variables

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Significance and Relevance

The heavy fraction of plastic pyrolysis oil can be efficiently upgraded at mild conditions over ZSM5-based catalysts yielding a liquid product with optimum composition in naphtha range as shown by the tests conducted specifically in batch reactors with n-hexadecane and 1-hexadecene as model compounds. The deposition of 2.15wt% Ru metal on ZSM5 proved beneficial for the activity, especially under hydrogen atmosphere.

Preferred topic: 1st Circular economy, 2nd Sustainable and clean energy production and transport
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Plastic recycling remains a challenge, with a substantial portion of recycled plastics ending up in landfills or polluting oceans. Several approaches for plastic recycling are under development nowadays with the more technologically mature that of mechanical recycling. However, plastics obtained from mechanical recycling methods are of lower quality and are characterized by higher unit production costs compared to primary plastics[1]. An alternative way of managing plastic waste is chemical recycling, with the pyrolysis process playing the major role. Pyrolysis can be a viable option as it can convert all types of plastics into a product mixture which can be either used as fuel or as source of monomers. However, the quality of the resulting oil is unsuitable to be directly used in existing steam cracking units necessitating selective upgrading[2]. Thermal upgrading hinders the conversion of heavy hydrocarbons due to the random decomposition mechanism and therefore the use of catalysts is recommended. It is well known that cracking reactions necessitate acidic functionalities on the catalyst surface while the presence of metals can further affect the mechanistic pathways[3]. This study aims to catalytically upgrade pyrolysis products by selectively decomposing the heavy fraction of pyrolysis oil into naphtha-range hydrocarbons. Two model compounds, namely a paraffin and an olefin with 16 C-atoms representing the light fronts of the heavy oil fraction, are employed in the study. The effect of phase (liquid or gaseous) under which the pyrolysis reactions proceed is explored by employing high pressure batch and atmospheric pressure fixed bed reactors and ZSM5-based catalysts.

Materials and Methods

The catalysts used were the ZSM5 (Si/Al=25) and the one promoted with 2.15 wt% Ru. The deposition of Ru was performed following the wet impregnation method with subsequent drying and calcination at 500°C for 3h. The experiments were conducted using batch and fixed bed reactors. The tests in the batch reactor were conducted at 300°C, high initial pressure 20bar (in N_2 or H_2 atmosphere) to ensure that the reactions proceed in the liquid phase while that of fixed bed at atmospheric pressure and temperature ranging from 250 to 350°C and W/F 0,4-0.9 $g_{cat}/mol_{C16}.h$. The analysis of gaseous and liquid products was performed employing four gas chromatographs equipped with suitable columns and detectors.

Results and Discussion

The conversion of n-Hexadecane at 300°C under batch conditions highly depends on the type of catalyst (Ru promoted or non-promoted ZSM5) and the gaseous atmosphere (N_2 or H_2) used. The presence of Ru and the reducing atmosphere favor the feed conversion which reaches 62wt% after 2h of testing (Fig 1a). The liquid products formed are highly paraffinic (n- and i-) in the range of C5-C11 and comprise ~90wt% of the total products (Fig. 1b). The gaseous products consist mostly of C3 and C4 with dominance of propane. The long residence time of the intermediates formed most likely enhances the H-transfer reactions leading thus to paraffinic compounds[4]. The liquid/gas selectivity remains almost constant irrespective of the catalyst and the atmosphere. Deposition of intermediates and coke like compounds was detected which however do not surpass 0.3wt% of the feed.

In the fixed-bed reactor operating at atmospheric pressure, reactions occur in gaseous phase. Increasing temperature from 250 to 350°C enhances total conversion to over 95 wt% at 350°C and 0.15 s residence time, especially in the presence of Ru/ZSM5 catalyst. Pyrolysis in the gas phase boosts cracking increasing selectivity towards gas products (C_3-C_4) from 40 to 60 wt% at the expense of liquid products which comprise of light hydrocarbons (C_5-C_7). Residence time, despite being very short (0.078-0.15s), linearly increases total conversion and productivity without changing the gas/liquids selectivity. The gaseous and liquid products formed are rich in alkenes with mostly iso and normal olefins accounting for 60 wt% of the products.

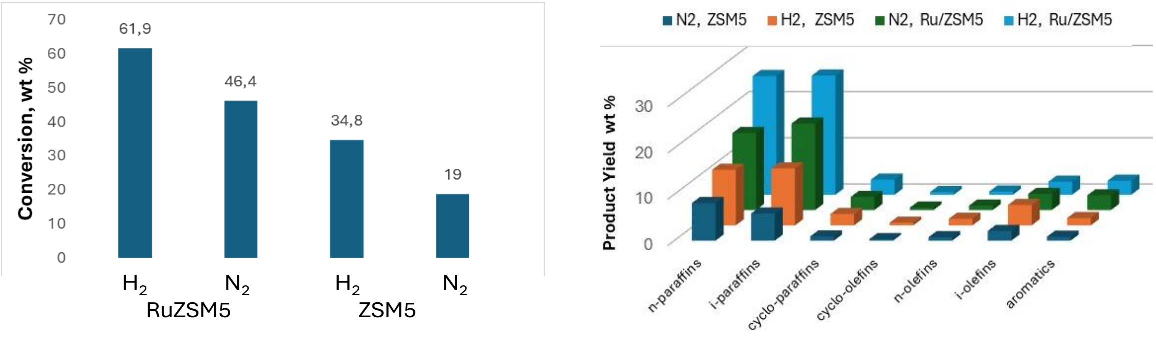

Figure 1 n-Hexadecane pyrolysis in a batch reactor at 300°C and 20 bar pressure as a function of catalyst and gaseous atmosphere a) wt% nC16 conversion b) wt% product yield distributed according to PIONA composition

Upgrading of plastic pyrolysis oil can effectively proceed under relatively low temperature around 300°C over ZSM5 based catalysts. The reactor type and the pressure, which determines the gaseous or liquid phase in which the reactions take place, have the main role in product selectivity. Hydrocarbons in the desired range of naphtha (90wt% of the products) with minimum olefinic content even in the absence of H_2 in the gas phase, are formed under batch conditions. The presence of Ru affects mostly the activity. In contrast, in the fixed bed reactor tests, n-Hexadecane, at similar temperatures, is almost fully converted to a hydrocarbon mixture C3-C7 with gases/liquids ~50% (wt) with olefins being the main constituents. Research activities are ongoing with 1-Hexadecene, as model compound, to explore the effect of the same parameters on catalytic cracking of the olefinic hydrocarbon.

References

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