

Production of aromatics from biomass: the reaction network and implications for catalyst deactivation

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Highlights

- The production of green aromatics from biomass-deriving compound is achieved.
- The complex network of products and its evolution with time is investigated in depth.
- The coke deactivating the catalyst is quantified and characterized.
- Product distribution and coke formation are linked in the same reaction network

1. Introduction

The production of aromatic hydrocarbons, specifically benzene, toluene and xylenes (BTX), is of utmost importance as they can be used as solvents and precursors for the production of polymers, pharmaceuticals, pesticides and many other compounds[1]. In this frame, manufacturing BTX from bio-derived raw materials represents a significant step forward in achieving independence from the non-renewable feedstock, as aromatics production nowadays is based only on carbon fossil feedstock. The most promising alternative green route is the Diels-Alder (DA) condensation of a diene and a dienophile, coming from biomass. This approach typically uses furan (the diene), which is cyclized with an olefin (dienophile) obtained by dehydration of an alcohol [2]. Although these chemicals can be derived from biomass, several steps are needed to obtain them. Recently Gancedo et al.[3], proposed an innovative approach to produce BTX starting from furfural (FFL) and ethanol (EtOH), which are obtained from biomass through a limited number of steps. Aromatization of FFL and EtOH involves dehydration, decarbonylation and condensation reactions that are catalyzed by solid acid catalysts. According to the literature, the catalysts of choice are zeolites, mainly with the MFI structure such as ZSM-5. The main issues associated with this process are selectivity towards BTX as well as deactivation by coke formation, which drastically shortens the catalyst lifetime. As this process, with this particular reagent choice is still quite unexplored in the literature, in-depth knowledge of the mechanism of formation of aromatics and carbon deposition is required to exploit this reaction from the viewpoint of a technological application. The aim of this work was to elucidate a complex network of products, still not reported in the literature, revealing how these products eventually lead to formation of aromatics which fused rings that selective poison the catalytic sites.

2. Methods

The zeolite catalysts were obtained by calcination of the ammonium forms provided by Zeolyst International. FFL was purified by distillation under vacuum prior to the catalytic experiments, whereas no pretreatment is needed for EtOH. The reaction was carried in a fixed bed plug-flow reactor working at 250-500°C at ambient pressure, with He as an inert gas to tune the residence time. The liquid products were analyzed with GC and Karl-Fischer titration, whereas the gas phase was analyzed with a micro-GC. The fresh and spent catalysts were characterized by nitrogen physisorption, pyridine adsorption, TGA, elemental analysis and electron microscopy.

3. Results and Discussion

In this work the effect of several parameters and features of the zeolite catalysts on the BTX production was investigated. In particular, the impact of the zeolite topology (BEA or MFI) as well as the influence of the Si/Al ratio and the nature (Brønsted or Lewis) and strength of acid sites are considered. Moreover,

the parameter space was explored by alteration of the reaction temperature, residence time and the feed composition. This gave a preliminary insight on the mechanism of formation of BTX and catalyst deactivation. A simplified scheme of the reactions involved and possible products are presented in Figure 1.

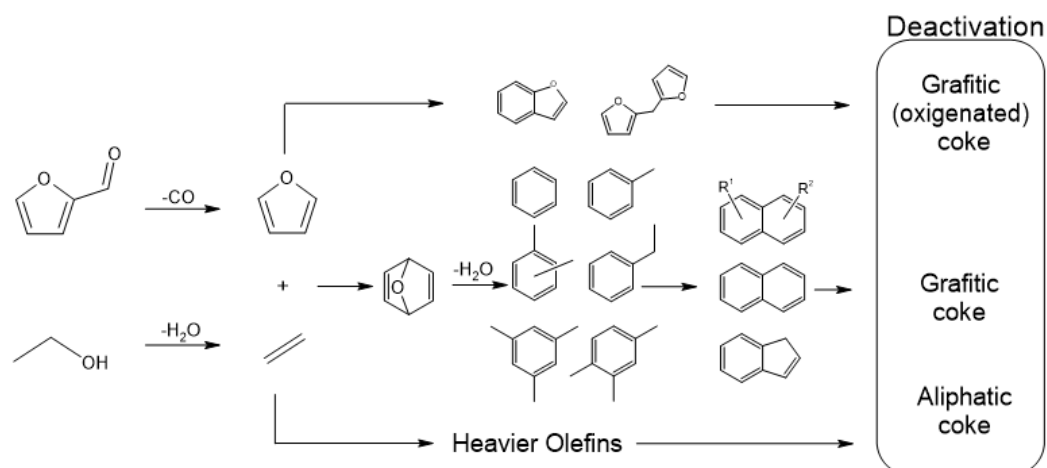


Figure 1. The reaction scheme for the synthesis of BTX from FFL and EtOH.

Preliminary studies demonstrated that HZSM-5 zeolites are the most active in the aromatization reaction, with the optimal Si/Al ratio being 40, while lower or higher Si/Al ratios are leading to fast catalyst deactivation or absence of production of aromatics, respectively. However, even with the most initially active catalyst the production of aromatics stopped after 4 hours of time-on-stream, with an evolution of the different aromatics over time, from benzene to multi-substituted and multi-ring aromatics. Conversely, deactivation in dehydration of EtOH and decarbonylation of FFL was less than 10% when compared to the initial conversion. This can be explained by the presence of the catalytic sites of different nature, whereas only a part of these is active in aromatization suffering from deactivation. In the same way as for aromatics, several other compounds are formed before selective deactivation, such as C2-C4 olefins and alkanes. The amount of coke deposits on the spent catalysts from experiments with single reagents (FFL or EtOH), is suggesting how FFL is generating higher amounts of grafitic coke (17.7 % w/w) leading to catalyst deactivation. On the other hand, EtOH generates lower amounts of coke (0.8 % w/w), that partially decompose at a lower temperature (ca. 200°C), and therefore it can be continuously removed under reaction conditions, maintaining the catalyst active.

4. Conclusions

In this work production of aromatics from furfural and ethanol was investigated, with a particular focus on the detailed analysis of different gas and liquid products and their evolution with time on stream. In fact, an evolution from gas products, to light and heavy aromatics in observed, eventually resulting in coke formation and selective deactivation of the catalyst. Detailed analysis of the product mixtures as well as physico-chemical characterization of the spent catalyst give insights on the complex reaction network and catalyst poisoning, and set the basis for the design of catalysts with longer life-time and easier regeneration.

References

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Keywords

Production of aromatics, catalyst deactivation, reaction network, mechanism of deactivation