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Model based analysis of the effect of ethylphenol addition to *n*-decane in fluid catalytic cracking over an extended zeolite library

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Highlights

- Ethylphenol in the feed induces steeper deactivation and gasoline selectivity increases
- Deactivation is more pronounced for faujasites with low mesoporous surface area
- Steeper deactivation is attributed to higher frequency factor for coke production
- Cracking to gasoline proceeds with higher frequency factor

1. Introduction

Fluid Catalytic Cracking (FCC) is one of the major processes in oil refining and the petrochemical industry. It is performed on an acid catalyst containing a zeolite as main active component and typically converts gasoils of low commercial value into high value products, i.e., gasoline and Liquefied Petroleum Gas (LPG) [1]. The 20-20-20 as well as the long-term 2050 targets that the European Union (EU) has set itself, necessitate a shift in the energy supply towards biomass and, within this framework, the co-feeding of HydroDeOxeygenated (HDO) bio-oils in a FCC unit. The large amount of phenols typically found in an HDO oil, due to their refractive character compared to other oxygenates renders this class of molecules into a highly relevant one as feed for co-FCC [2]. In this work, we investigate the catalytic cracking of *n*-decane (C10) purely, representing the conventional gasoil feed, and in admixture with 2-ethylphenol (EP), as a model component for HDO bio-oil, over a series of faujasites. An FCC kinetic model has been developed to assess the obtained data and account for the observed effects of the EP addition in the FCC feed.

2. Methods

The FCC testing of C10 (pure or with 10wt% EP) was conducted in a continuous flow fixed-bed quartz reactor. Twelve faujasites with varying Si/Al ratio and 200-315 mm particle size were investigated in experimental runs of 25 hours (TOS=25 h). The deployed dry weight of the catalyst was 600 mg. The operating catalyst bed temperature and pressure were fixed at 753 K and 1 atm respectively. The feed gas mass flow rate was fixed at 50 mg/h. All the investigated materials were characterized with respect to their concentration of Brønsted and Lewis acid sites as well as their micro- and meso-porous volume and surface area.

The experimental data were assessed using a five-lump model, the lumps being defined according to their carbon number and boiling point ranges, namely the gas oil (consisting either of pure C10 or of a mixture 10wt% EP in C10), the gasoline (C5-C9), the coke, the LPG (C3-C4) and the dry gas (C1-C2). These five groups were incorporated in the reaction network that is depicted in Fig. 1[3] and the involved kinetic equations were embedded in an isothermal plug-flow reactor model with transient behavior. Apart from the main kinetics, the model also includes individual, selective deactivation functions which relate the catalyst coke content to the activity of the catalyst for each reaction between the lumps. The adjustable parameters comprised frequency factors, activation energies and deactivation factors for quantifying the reactions depicted in Fig.1.

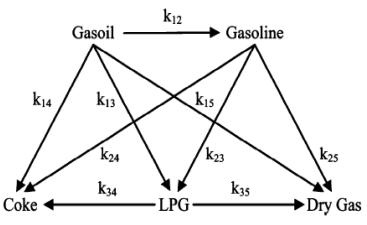

Fig.1 Schematic of the 5-lump FCC model

3. Results and Discussion

During the FCC testing, it was observed that the addition of EP in the feed, even at a percentage as low as 10wt%, induces a faster deactivation of the employed faujasites. This behavior was more pronounced over materials with low mesoporous surface area (and/or volume), probably due to the more pronounced effect of coke not being able to be accommodated in these pores and, hence, more rapidly blocking the pore network. Correspondingly, the increase in gasoline selectivity and decrease in LPG selectivity with TOS over all the investigated faujasites were more pronounced in the presence of EP. The above findings in the case of two of the best performing materials, i.e., CBV720 and 360HUA, are depicted in Fig.2 and Table 1. The FCC kinetic model was employed to quantify the information contained in the experimental data on the effect of EP co-feeding on conversion and selectivities. Higher frequency factors, by 50 % for CBV720 and 800% for 360HUA, were obtained for the feed conversion into coke in the presence of 10 wt% EP. This effectively accounts for the observed steeper deactivation of the investigated materials with TOS, which is significantly more pronounced for 360HUA, in particular at low TOS, see Fig.2. For the reaction of gasoil to gasoline, approximately 10 % higher values for the frequency factor were calculated for both materials in the case of the combined feed which stems from the sharper increase of gasoline selectivity with TOS, see Fig.2.

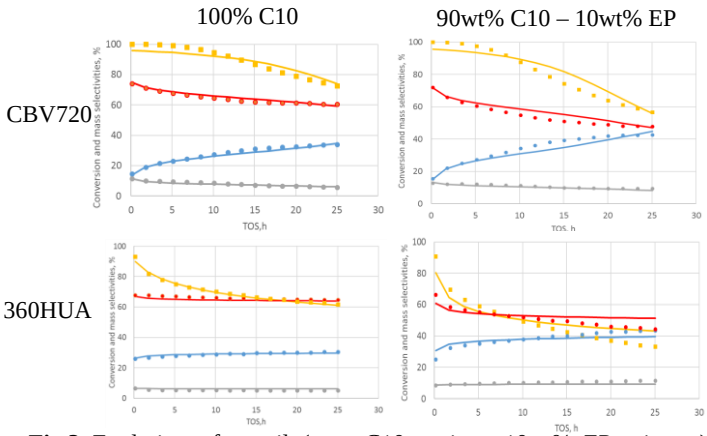

Fig.2 Evolution of gasoil (pure C10 or in a 10wt% EP mixture) conversion and product selectivities with TOS. Yellow: gasoil conversion; blue: selectivity to gasoline; red: selectivity to lpg; grey: selectivity to dry gas. Symbols : experimental points, lines: calculated results by employing the model.

Table 1. Surface area of faujasites, m^2/g

	CBV720	360HUA
mesopore	263	123
micropore	623	609

4. Conclusions

The effect of oxygenates containing HDO bio-oil admixture with an FCC feed was investigated on faujasite zeolites in a fixed bed reactor with feed either pure C10 or in a mixture with 10wt% EP. It was observed that EP induces faster deactivation with TOS, which was more pronounced when materials with low mesoporous surface area were employed. The gasoline selectivity was also shown to increase more steeply with TOS for an EP containing feed. With the aid of a 5-lump FCC kinetic model, the above trends were rationalized by an increase in the value of the frequency factors, related to the feed conversion into coke and gasoline.

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Keywords
Fluid Catalytic Cracking; faujasites; kinetic modelling; deactivation