

## Study of the tetralin conversion to BTX for LCO upgrading purposes

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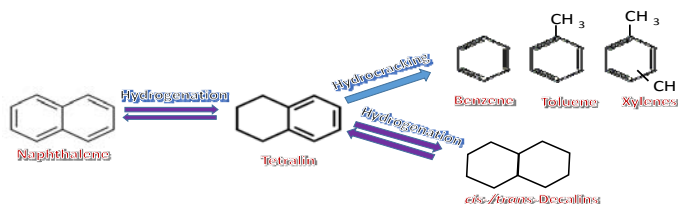
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### Highlights

- Tetralin conversion to BTX requires of both metal and acid functions.
- Zeolite and metal catalysts were tested alone and in four solid mixtures.
- High Brønsted acidity favored the BTX formation but reduced the catalyst life.
- A mixture of catalysts produced acceptable BTX selectivity and low deactivation.

### 1. Introduction

Light cycle oil (i.e. LCO) is a low quality middle distillate coming from the Fluid Catalytic Cracking unit. It contains relatively large amounts of sulfur (i.e. up to 4 wt.%), nitrogen (i.e. up to 1,000 wt.ppm) and aromatics (i.e. up to 75 wt.%) [1]. Aromatic compounds are mainly diaromatics (i.e. Naphthalene derivatives). An attractive alternative for LCO upgrading is the production of high commercial value monoaromatics such as benzene, toluene, and xylenes (i.e. BTX), by means of a process involving hydrogenation and hydrocracking steps, as represented in the Scheme 1 [2,3].



**Scheme 1.** Reaction pathways involved in the formation of BTX.

It has been reported that the tetralin conversion to BTX requires both acid and metal functions [3]. The first one for favoring hydrocracking reactions, the last one for reducing the presence of by-products and coke formation that eventually lead to the deactivation of the catalysts. Consequently, product selectivity and catalyst life in terms of deactivation rate, should be studied by varying the amounts of acid (i.e. ZSM-5) and hydrogenation (i.e. NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) commercial catalysts, at given experimental conditions.

### 2. Methods

1,2,3,4-tetrahydronaphthalene (i.e. Tetralin, Sigma Aldrich) and ultra-high purity hydrogen (i.e. 99.99 vol.%, Infra-México) were used in the tests. ZSM-5 had the following properties: H-form; SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>: 34 mol/mol; crystal size: < 1  $\mu$ m; pore diameter: 0.53 x 0.56 / 0.51 x 55 nm, shape: 2 mm beads; Brønsted and Lewis acidity at 400 °C: 23 and 28  $\mu$ mol Py/g, respectively. NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (i.e. Ni: 3.0–4.5 wt.%; Mo: 10.0–20.0 wt.%) had the following properties: Bulk density: 0.63–0.70 g/cm<sup>3</sup>; pore volume: 0.58–0.65 cm<sup>3</sup>/g; BET area: 180–250 m<sup>2</sup>/g; Brønsted and Lewis acidity at 400 °C: 2 and 76  $\mu$ mol Py/g. The tetralin conversion to BTX was performed in a bench-scale setup equipped with a fixed-bed trickle reactor (i.e. Vol.: 10 mL; Internal diameter: 1 cm), which was operated in the down-flow mode.

Prior to be loaded into the reactor, the catalysts were dried in an oven at 120 °C for 1.5 h. The NiMo and ZSM-5 were tested alone and in the following NiMo/ZSM-5 mixtures: 20/80, 30/70, 40/60 and 50/50 vol/vol.

The NiMo catalyst was activated in-situ for 18 h using a desulfurized naphtha spiked with 1.5–2.5 wt.% of DMDS at Temperature: 210–315 °C; Pressure: 4.0 MPa; Liquid Hourly Space Velocity (i.e. LHSV): 1.0 h<sup>-1</sup>; and Hydrogen/Hydrocarbon (i.e. H<sub>2</sub>/Hc) ratio: 315–378 m<sup>3</sup>/m<sup>3</sup>.

After the activation step, operating conditions were adjusted to the corresponding experiment: Temperature: 400 °C; Pressure: 4.9 MPa; LHSV: 1.72 h<sup>-1</sup>; H<sub>2</sub>/Hc: 372 m<sup>3</sup>/m<sup>3</sup>; Operating time: 48 h. The reactor effluent was sent to a vapor-liquid separator, where the rich-hydrogen stream was analyzed by gas chromatography and the liquid stream from the bottom was collected in a metal container, weighted for mass balance purposes and characterized in a FID-GC Bruker, by comparing the retention times with standard mixtures of the hydrocarbons involved. Selectivity and deactivation were calculated just dividing the amounts of BTX and by-products by the initial amount of tetralin.

### 3. Results and discussion

The results are shown in Figures 1a and 1b. The BTX selectivity and deactivation rate increased as the amount of ZSM-5 increased. However, it seems that the 50/50 vol/vol NiMo/ZSM-5 mixture presented an adequate balance between an acceptable BTX selectivity (i.e. Close to 40%, Fig. 1a) and the deactivation rate (i.e. 0%, Fig. 1b) for the time frame studied (i.e. 48 h). The NiMo/ZSM-5 system may hydrocrack tetralin into BTX and hydrogenate coke precursors, reducing catalyst deactivation rate.

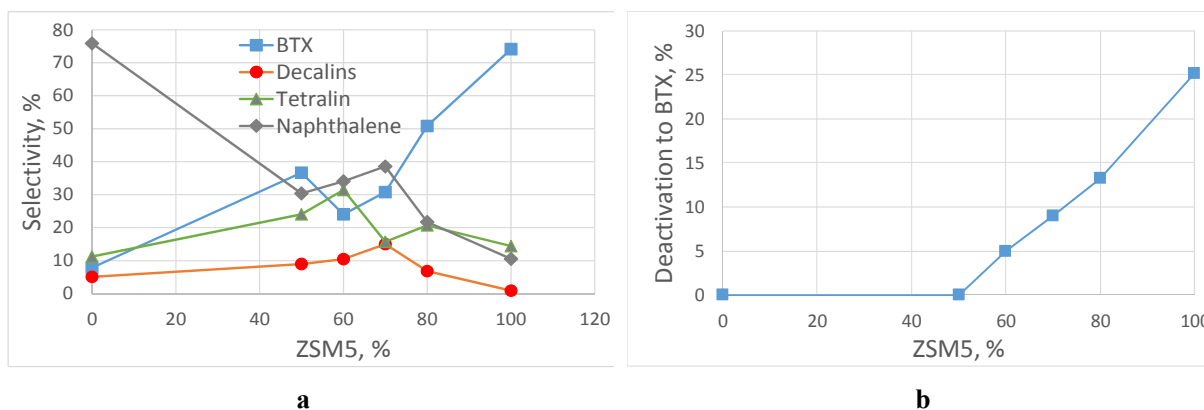


Figure 1. Effect of the ZSM-5 in the NiMo/ZSM-5 mixtures for: a) Selectivity, b) Deactivation rate.

### 4. Conclusions

The conversion of tetralin to BTX requires both acid and metal functions and a proper balance between them in order to acquire high selectivity and low deactivation rate. Based on the results included in this work, a BTX selectivity near to 40% and minimal deactivation rate can be achieved with a 50/50 vol/vol mixture of NiMo and ZSM-5 catalysts at given experimental conditions.

### References

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### Keywords

BTX, Tetralin, ZSM-5, LCO.