

Is there a synergistic effect between FT and MTH processes?

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Introduction

The most important routes for the synthetic production of liquid hydrocarbons are the methanol-to-hydrocarbons (MTH) [1] and Fischer-Tropsch (FT) synthesis. The MTH process is characterized by the presence of olefins and aromatic compounds in the products, whereas, FT yields mainly linear paraffins.

So far, only one patent has claimed that the use of trifunctional catalytic systems formed by a physical mixture of a Fischer-Tropsch catalyst, a methanol synthesis catalyst and a methanol conversion catalyst (zeolite) would be able to completely modify the product distribution of both MTH and FT processes, leading to hydrocarbons in the gasoline range (C₅-C₁₂) with improved selectivity and low aromatic content [2].

In this contribution we discuss a synergistic effect among these reactions and also the role of the methanol conversion catalyst (zeolites) considering its acidity and morphology.

Materials and Methods

The reactions were carried out using a physical mixture of three components: 1- a Fischer-Tropsch synthesis catalyst (FT), composed by Fe, Ca, K and Al, prepared by coprecipitation; 2- a commercial methanol synthesis catalyst (MS), composed by Cu, Zn, Al and 3- a zeolite (HZSM-5) as a methanol conversion catalyst (MTH process). Two dealuminated Y zeolites (DAZ2 and DAZ3), prepared and described by Sobrinho et al. [3] were also employed in order to verify the acidity and structure influence. The following ratio among the catalysts FT:zeolite:MS = 1.0:1.5:4.5 was employed. The catalyst mixture was treated at 523K with a H₂ (5%)/He flow during 36h. The reaction was carried out at 504K, 34atm using H₂/CO = 2 and GHSV=900h⁻¹. The acidity of the methanol conversion catalysts was evaluated by chemisorption of n-butylamine at 373K followed by thermal analysis. When one of the components was missing, SiC was used in the catalyst mixture.

Results and Discussion

Table 1 displays the conversion and products distribution for three distinct catalysts mixtures. It can be observed that the product distribution and the activity of the systems depend on the nature of the mixture. In the case of HZSM-5 + MS, it was noticed that only the methanol synthesis and the dehydration reaction were working, as nothing but methanol and DME were identified as products. Moreover, the mixture of FT + HZSM-5 shows a very low activity. On the other hand, the physical mixture of the three catalysts (FT+HZSM-5+MS)

shows the highest CO conversion and the formation of hydrocarbons from C₁ to C₁₂. The aromatics concentration was less than 2% of the products and the conversion was stable during the experiments (around 6 h). The results show that there is a synergistic effect when using this physical mixture. It could also be observed that the selectivity to DME decreases after 1h on stream, while the other products increase slightly, suggesting that this ether is an intermediate compound of this process, which is a characteristic of the MTH reactions.

Table 1. CO conversion (X_{co}) and products distribution of different catalyst mixtures

| Mixture | X _{co} % | Products distribution wt.% (free of CO ₂) | | | | |
|---------------|----------------------|-------------------------------------------------------|--------------------|-----------------|--------------------------------|---------------------------------|
| | | DME | CH ₃ OH | CH ₄ | C ₂ -C ₄ | C ₅ -C ₁₂ |
| FT+HZSM-5+MS | 57 | 34 | 14 | 15 | 29 | 9 |
| FT+HZSM-5+SiC | 2 | - | - | 51 | 49 | - |
| SiC+HZSM-5+MS | 23 | 89 | 11 | - | - | - |

Table 2 shows the influence of the zeolite in the activity of the mixture and products distribution. Presenting the same structure but distinct acid strength distribution, DAZ2 and DAZ3 behaved in the same way suggesting that acid strength is not relevant in this condition. On the other hand, the results related to HZSM-5 (conversion, DME and methanol concentration) when compared with DAZ1 and DAZ2, suggest that the zeolite structure plays an important role in the conversion and the selectivity of the system. Considering these results, and also behavior of the FT catalyst (Table 1) it can be suggested that the MTH process seems to play the major role in this synergistic effect.

Table 2. CO conversion (X_{co}), products distribution and acid proprieties of different zeolites.

| Mixture | X _{co} % | Products distribution wt.% (free of CO ₂) | | | | | MAS* | SAS* |
|--------------|----------------------|-------------------------------------------------------|--------------------|-----------------|--------------------------------|---------------------------------|------|------|
| | | DME | CH ₃ OH | CH ₄ | C ₂ -C ₄ | C ₅ -C ₁₂ | | |
| FT+HZSM-5+MS | 57 | 34 | 14 | 15 | 29 | 9 | 0.3 | 1.0 |
| FT+DAZ2+MS | 80 | 3 | 18 | 22 | 40 | 18 | 1.4 | 1.0 |
| FT+DAZ3+MS | 79 | 3 | 19 | 19 | 40 | 20 | 1.8 | 0.4 |

*MAS: amount of weak and medium acid sites (mmol.g⁻¹) obtained by n-butylamine desorption in the range of 30-330°C, SAS: strong acid sites (mmol.g⁻¹), obtained by n-butylamine desorption in the range of 330-520°C.

Significance

This contribution discusses, for the first time, the synergistic effect between FT and MTH processes. The association of these processes renders the production of synthetic gasoline with low aromatic content from coal, natural gas and biomass residues possible.

References

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