



Steam catalytic cracking of naphtha over ZSM-5 zeolite for production of propene and ethene: Micro and macroscopic implications of the presence of steam

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ABSTRACT

One option to produce more ethene and propene can be to crack naphtha type fractions in dedicated smaller FCC units. We present here the results obtained for high temperature steam catalytic cracking (SCC) of a representative naphtha product (*n*-heptane) with ZSM-5. It has been found that under those conditions the presence of steam produces an irreversible dealumination of the zeolite as well as a reversible deactivation due to the interaction of water with active sites with a negative effect on protolytic cracking. A kinetic decay model that takes into account the two phenomena has been developed. The apparent activation energy is lower in the presence of steam. It appears that whilst the presence of steam is vital when processing heavy feeds to achieve a better feed dispersion and a more effective catalytic cracking in conventional fluid catalytic cracking (FCC) units, in the case of steam catalytic cracking of naphtha (*n*-heptane) the presence of steam has a negative effect on the final performance of the catalyst. On the other hand, whilst steam does not modify ethene and propene selectivity, significantly decreases H₂ and CH₄ formation, as well as formation of potential coke precursors.

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1. Introduction

The demand of light alkenes, i.e., ethene and propene is expected to keep increasing in the near future. They are mainly obtained by steam cracking (SC) and from fluid catalytic cracking (FCC) units, especially in the case of propene [1]. Indeed, whilst in the case of conventional FCC it is possible to produce some ethene, the ratio of propene to ethene is, generally, very large. This is not the case for SC in where the high reaction temperature favours the formation of large amounts of ethene. However, with increasing use of methane and ethane in the feed of SC units it has been a decrease in the ratio of propene to ethene [1,2], that requires to produce more propene from other processes.

It is possible to regulate the ratio of propene to ethene obtained during cracking, whilst producing significant amounts of ethene, by a catalytic cracking process that operates at temperatures in between those of FCC and SC [3]. In this sense it has been recently developed a FCC technology that operates under more severe conditions, in where the catalytic cracking of, for instance, vacuum gasoil, takes place at higher temperatures (~920 K), lower contact time, and larger amounts of steam that promote a better dispersion of feed and reduce coke selectivity [4]. Nevertheless, these more

severe operating conditions will require low cost more hydrothermally stable catalyst with low hydrogen transfer activity.

For accomplishing all the above demands one can certainly think on FCC cracking catalysts and units able to process vacuum gasoil, or even heavier feeds, that whilst achieving high conversion can, at the same time, increase the yield of propene and ethene [5,6]. Nevertheless, one may also consider to use smaller FCC units able to crack naphtha and other relatively light feeds at high temperature, high catalyst to oil ratios, shorter contact times and in the presence of steam. In other words, these smaller FCC units will operate under conditions closer to those of steam cracking. If in the case of processing vacuum gasoil one can think on a highly steam stable FCC catalyst containing small crystallite size USY zeolite together with highly stable ZSM-5, for cracking naphtha the zeolite of choice could be highly hydrothermally stable ZSM-5 zeolite.

We have studied here the second option by following the catalytic cracking of naphtha (C₇–C₁₂ *n*-alkanes) under high severity operation conditions. It includes high reaction temperatures and large amounts of steam in the feed to increase the production of ethene and propene. As catalysts we have used a series of ZSM-5 zeolites with different chemical composition. In the first part of a broader study, we have used a unique reactor set that allows to take and analyse instantaneous samples from very short to longer times on stream (TOS). The system allows us to study the effect of coking and steam on the initial activity and selectivity of the catalyst, as well as their evolution with time. This also gives information

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