



# Stabilization of ZSM-5 zeolite catalysts for steam catalytic cracking of naphtha for production of propene and ethene

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## ABSTRACT

In order to increase ethene and propene, naphtha steam catalytic cracking has been considered. The cracking of C<sub>5</sub>–C<sub>12</sub> *n*-alkanes with ZSM-5 has been studied in absence and in presence of steam and the influence of the operation variables was studied. Irreversible catalyst deactivation by dealumination also occurs in the reactor when the cracking is carried out in the presence of steam. To diminish steam deactivation, the influence of zeolite Si/Al framework and a postsynthesis treatment by phosphorous have been studied and optimized. Much more stable catalyst can be achieved that result in an increase in activity without penalty for production of ethene and propene.

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## 1. Introduction

There is much incentive to increase the yield of propene and ethene during fluid catalytic cracking (FCC) operations [1]. This is normally done by introducing a medium pore zeolite (ZSM-5), as an additive, which cracks gasoline to produce mainly C<sub>3</sub> and C<sub>4</sub> gases with a high selectivity to propene and butenes [2–5]. The increase in propene production is directly proportional to the amount of ZSM-5 introduced in the unit, until reaching almost a plateau for 5–10 wt% of zeolite additive. However, the introduction of ZSM-5 in the FCC unit has little impact on the production of ethene, being the yield to this product mainly controlled by reaction temperature. This is the reason why ethene production relies mainly on high temperature steam cracking ( $T \geq 973$  K). Therefore, if the objective is to further increase production of propene and ethene by catalytic cracking, the FCC unit should operate at higher temperatures than it normally does. This however is not always possible due to thermal limitations of the materials in the regenerator, and compressor limitations. There is another option that considers the construction of dedicated smaller FCC units able to crack naphtha and other feeds at temperatures of 923 K and above [6]. In other words, these dedicated units will be working at temperatures closer to those of

steam cracking, in a type of operation that could be named as steam catalytic cracking (SCC).

If one refers to SCC as an FCC working at temperatures close to 973 K, it becomes evident that for this type of operation the catalyst should be heated at very high temperature in the regenerator during coke burn off. However, the amount of coke produced during cracking of naphtha, or similar feeds, is too low to produce by combustion the catalyst temperatures required in the reactor. Therefore extra heat will have to be supplied into the regenerator by burning off added hydrocarbons as, for instance, fuel gas.

In any case, cracking hydrocarbons at high temperatures in the presence of steam, as well as heating the catalyst at very high temperatures in the regenerator, will have an important impact on catalyst stability. Indeed we have seen that when performing steam catalytic cracking at temperatures of up to 973 K, the ZSM-5 zeolite suffers an important permanent deactivation due to a continuous dealumination process [7]. Therefore, for carrying out high temperature FCC and high temperature SCC it will be mandatory to prepare highly hydrothermally stable zeolite catalysts and, more specifically, highly hydrothermally stable ZSM-5 zeolite. Nevertheless, the higher stability should preferentially be achieved without sacrificing the yields to ethene and propene.

In the present work we have studied this issue by performing the SCC of a series of naphtha molecules (C<sub>5</sub>–C<sub>12</sub> *n*-alkanes), with ZSM-5 based catalysts. As expected, a conventional ZSM-5 zeolite dealuminates very fast leading into an important permanent

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