TEMPERATURE EFFECT ON DEACTIVATION OF ZSM-5 ADDITIVES IN FCC PROCESS

A. Gusev[1], A.Psarras[1], M.Papapetrou[1], D.Iatridis[1], E. Heliopoulou[1], A.A.Lappas[1,*]
[1]Chemical Process and Energy Resources Institute,
Center for Research and Technology Hellas (CPERI/CERTH)
***angel@cperi.certh.gr**

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ABSTRACT

Zeolites are widely used in various catalytic applications, while especially ZSM-5 zeolites are broadly used in several important reactions in the petrochemical industry due to their high activity and shape selectivity [1]. Fluid catalytic cracking (FCC) is one of the most important processes in a modern refinery as it provides almost 50% of the total gasoline pool, while utilization of ZSM-5 based additives in the FCC process has increased sharply the last few years. Application of ZSM-5 catalytic additives to the FCC process enhances the conversion of olefins in the gasoline boiling range (C5 to C12), formed during Y zeolite cracking, to olefins in the LPG range (C3 and C4s), that are very important raw materials in the petrochemical industry [2-4].

During the FCC process the catalyst is subjected to continuous recirculation between the riser, where cracking reactions take place, and the regenerator where coke deposited on the catalyst during cracking is burned off. Regeneration environment includes high temperatures and the presence of steam, which lead to the hydrothermal deactivation of the zeolitic components of the FCC catalyst. Activity loss is strongly related with the dealumination of the zeolitic framework and the consequent decrease of Brönsted acidity. Preventing or minimizing dealumination and therefore activity loss is a major research topic in zeolite utilization for FCC applications [5]. Steam dealumination of ZSM-5 zeolites has been quite often studied in the literature, while introduction of phosphorous to increase the attrition resistance of catalyst particles led also to increased hydrothermal stability of ZSM-5 zeolite additives by inhibiting framework dealumination [6-8]. Currently P is considered as a standard component of most FCC and ZSM-5 catalysts/additives.

In addition to the above the deactivation and testing of ZSM-5 additives is a complicated issue. This is validated by the fact that different laboratories use different procedures to deactivate and evaluate these additives. Regarding ZSM-5 additives evaluation the various laboratories use their standard evaluation procedure followed for the FCC catalysts. Fixed bed MAT units, fluid bed units, ACE unit or pilot plant units have been used in literature. However, based on CPERI experience the pilot plant testing is the most reliable tool for correct evaluations. the majority of the laboratories use steam deactivation of different temperature, time and steam percent severity. The steaming temperature range varies from 760-815°C, the time from 5 to 24 hrs while the steam percent from 50 to 100%.

In this research work we have investigated the effect of steaming temperature on ZSM-5 zeolites deactivation. The work was carried on a bench scale steaming unit using different hydrothermal severities. The steaming temperature was the main parameter keeping constant the steam partial pressure and the steaming time. In the study we used a commercially available ZSM-5 additive. The additive was steam deactivated at the temperature of 815°C and 840°C for 24 hrs at the presence of 100% steam. The deactivated samples were fully characterized using BET for surface area and FT-IR for Bronstend and Lewis acidity. Moreover, the fresh ZSM-5 sample was also fully characterized.

Our FT-IR results have shown that the deactivation temperature plays a tremendous role on the acidity of the ZSM-5 deactivated samples. In comparison with the fresh samples the temperature treatment at 815^{o}C dropped the concentration of Bronsted acid sites for 90%. For the case of Lewis acid sites the decrease was for 80%. Except for the fact that temperature affects on acid sites decrease we have the evidence that the temperature affects more on Bronsted than Lewis acid site. This was clear when the

results of FT-IR, for 840 ^{o}C treated sample, were examined. The concentration of Bronsted acid sites decreased further for 60% whereas in case of Lewis sites the decrease was for 26%. The affect is of the same order of magnitude for both cases but for the case of Bronsted acid site the effect is stronger.

BET analysis shown that the surface area is practically unchangeable with the temperature. This means that the temperature does not affect on the morphology of the catalytic particles. Thus the morphologic factor is not the reason for the acidity decrease. All ZSM-5 deactivated samples were also tested in a fluid bed testing unit. In the paper we will present the activity and selectivity performance of the deactivated samples and we will correlate this activity with the acidity of the samples.

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