



Silica poisoning in HDT catalysts by light coker naphtha

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ABSTRACT

γ -Alumina-based HDT catalysts used as silicon traps adsorb more efficiently silicon compounds from naphtha till saturation, which occurs at a relatively low concentration (5–10 wt%). As the silicon content in the catalyst increases, the surface is progressively deactivated, mainly affecting the hydrodenitrogenation and hydrogenation activity. According to the aforementioned, the deactivation of HDT catalysts was investigated by means of a fraction of naphtha doped with silicone oil with different concentrations, which was used to contaminate the catalysts. The presence of silicon species was detected by ²⁹Si NMR and FTIR spectroscopies. The Si–O–Al formation was evidenced by the B/L ratio measured for the doped HDT catalysts. The results obtained for the deactivation of HDT catalysts exposed to high silicon contents show that this factor plays a major role in the loss of activity.

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1. Introduction

Projections indicate that a high world-wide demand of engine fuels derived from oil refining will prevail for several years. This fact makes that oil refiners search continuously for the most energy efficient and cost-effective operations, especially for processing the less expensive and more available heavy crude oil. Actually, nowadays, the most efficient and productive oil refineries are configured around bottom-of-the-barrel processes, which lead to produce light fractions of hydrocarbons by upgrading oil residues. Process technologies include thermal cracking (visbreaking, thermal cracking, coking, etc.) and the delayed coking (DC) process.

DC is a thermal cracking process that upgrades crude oil vacuum distillation bottoms into gas and liquid products such as gas oil and naphthas, leaving behind a solid concentrated carbon material known as petroleum coke. The integration of the DC products, especially light naphtha (DCLN) fractions, into the processing structure of a petroleum refinery is quite challenging because of the high amounts of contaminants that they contain. Due to their origin, sulfur and nitrogen compounds, as well as olefins and diolefins are found in such high amounts that make hydrotreatment units (HDTUs) difficult to operate. Olefins and

diolefins are both gum and coke precursors, especially at high temperatures [1].

DC units use silicon polymers (antifoaming) that are added to the coker drums in order to suppress foaming that is generated by the light gases that are produced. As a consequence of the high temperatures that prevail in DC operation, silicon polymers decompose to form lighter silicon compounds that distil mainly with the naphtha product. Thus, silicon compounds are carried downstream to the HDTUs with the DCLN feed.

The goal of DCLN HDTUs is to provide the catalytic reforming units with a naphtha feed that must comply with very tough specifications in order to prevent troubleshooting or poisoning, and premature deactivation of the very expensive noble-metal-based catalysts used therein. DCLN HDTUs have to deliver naphtha with essentially no silicon since this is a very strong and permanent poison for the reforming catalysts.

This is readily accomplished by both specially designed catalysts and process configurations.

Only a few studies discussing technological and basic aspects of DCLN hydrotreatment have been published [1,2]. Breivik and Egebjerg postulated that hydroprocessing of DCLN fractions require specialized catalysts and technology to overcome the challenges of yielding a product within environmental specifications. They found that polydimethylsilanes (PDMS) readily decompose at high temperatures to form a series of cyclic siloxanes that are easily adsorbed on the alumina surface of the HDT catalyst. They suggested that silicon is present under the form of modified silica gels partly

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