
Question 46: Silicon uptake on hydrotreating catalysts is an increasing problem. (1) What operating conditions favor maximum silicon pickup by the catalyst? (2) Are there differences between silicon from coker antifoams and other sources? (3) Does the presence of other contaminants such as nickel and vanadium affect the silicon pick-up by the catalyst? (4) What best practices are you using to monitoring silicon pick-up by the catalyst?

James Esteban and Jeff Pro (Criterion Catalysts & Technologies)

Silicon in feed streams to Hydroprocessing units can pose a threat to catalyst performance and must be properly managed. Silicon acts as a poison to the catalyst by depositing on the surface of catalyst particles blocking active sites and reducing critical HDS and HDN activity. Silicon can be found in a wide range of feed streams and is a concern for all hydrotreaters processing naphtha, distillates, and vacuum gas oils. Silicon is present in crude fractions as well as Coker feeds where Si-containing anti-foam additives are widely used. Si from crude fractions is found in higher concentrations in synthetic crudes which have been manufactured at upgrading facilities which employ the use of delayed coking processes that use Si-based anti-foams. Regardless of the source, the methods employed to remove silicon are similar. Synthetic crudes can also contain Si from sand and aluminum silicate clays. In order to properly protect active catalyst beds from Si poisoning consideration must be given to the process conditions, catalyst selection, as well as feed components. In general Si uptake is maximized by operating at temperatures above 550 F with peak uptake performance above 600 F.

For units in naphtha service the temperature regime may limit the uptake capacity of the lead catalyst beds especially when considering units that have low temperature di-olefin reactors. In distillate and heavier service, the typical operating temperature regime is high enough to support maximum Si uptake performance. Another process condition impacting the Si uptake of a catalyst system is space velocity. Units that operate at high space velocities see a lower efficiency in terms of overall Si uptake as a percentage of maximum saturation capacity due to the high space velocity stretching the distribution profile of Si in the catalyst bed.

Catalyst properties such as surface area and particle size play a key role in the Si uptake performance of the catalyst system in lighter feeds like naphtha and distillate boiling fractions. In the gas phase, as in NHT (naphtha hydrotreating) service, catalyst surface area is a critical property that determines the catalysts' ability to uptake Si. Higher surface area catalysts will have a higher Si uptake capacity for NHT service; however, they will typically have less overall HDS/HDN activity due to a limited number of active metals present on the catalyst. This is of particular concern in units that operate at high space velocities with limited catalyst volume. In these cases, dual-function catalysts that have high Si uptake capacity in addition to high HDS/HDN activity can be employed to provide the required balance of Si uptake and activity. In addition to surface area, catalyst particle size is an important factor to consider. In NHT service the rate limiting step is diffusion, which implies that smaller particle catalysts will perform better

than larger particle catalysts in terms of Si uptake. The drawback to smaller catalyst particle size is a potential increase in pressure drop.

Units processing distillates benefit from the same catalyst properties but tend to be less affected by space velocity since these units are typically larger and hence have lower space velocities than naphtha units. Distillate units typically processing SR and light coker gas oils also do not have as high a feed Si content as naphtha units (especially naphtha units running high percentages of Coker naphtha). Units processing heavier feeds often contain other poisons such as Ni and V and hence require additional functionality. The catalysts also need sufficient active metals to promote the HDM reactions required for these larger molecules. Ni and V in high concentrations can reduce the Si uptake of trap catalysts; however, the Ni and V uptake is typically of greater concern.

For all applications, care should be taken to apply the appropriate catalysts for the service to optimize metals uptake with activity requirements.

In terms of monitoring Si uptake and performance one must employ a complete cradle to grave approach. Initially the catalyst system must be designed to ensure that there is adequate Si uptake capacity. With limited information in the design stage, employing the use of proper efficiency factors is critical to prevent Si slip to product streams above the desired specification. In some applications Si slip can be absolutely detrimental such as a NHT upstream of a catalytic reformer which uses very costly platinum promoted catalyst that can be poisoned by Si. Alternatively in other processes some Si slip to product is acceptable such as the treating of fractions for the blending of pipeline quality synthetic crudes. It is critical that refiners work closely with catalyst suppliers to ensure that objectives are clear, and the proper approach is applied. It is a best practice to refer to proven commercial performance when designing an optimized system and is best to make use of unit specific performance when available.

During the catalyst cycle, the catalyst activity and Si uptake should be continuously monitored during periodic unit performance reviews. It is best practice to monitor feed Si content using a method such as routine composite samples – these results can be used to calculate a projected Si accumulation which can be tracked against the maximum uptake capacity. Following the completion of the catalyst cycle spent catalyst samples should be collected to provide insight on actual catalyst performance versus predictions as well as to develop a Si distribution profile and material balance across the reactor and validate the accuracy of the composite feed samples. This methodology was well documented in an article – “Estimating silicon accumulation in coker naphtha hydrotreaters.” [1]

[1] Thienan Tran, Patrick Gripka and Larry Kraus, “Estimating silicon accumulation in coker naphtha hydrotreaters”, *PTQ, Catalysis* 2012.

Brian Watkins and Charles Olsen (ART)

Silicon is probably the most widespread catalyst poison encountered in hydrotreater feeds. The main source of silicon is from delayed coker operations that use an anti-foam agent based on polydimethylsiloxane to suppress foaming in the coker drums. The siloxane complex breaks down in the coking process to primarily cyclic methylsiloxane trimers. These species are volatile at coker temperatures with boiling points ranging from 270-475°F (132-246°C). As a result, these compounds

tend to concentrate in the overhead products, and as a general rule of thumb, 70-80% of the silicon at the coker ends up in the coker naphtha fraction. More recently, even refineries that do not have cokers are experiencing silicon poisoning of hydrotreating catalysts once thought unlikely since their feed source comes directly from the refiner's crude unit. These refineries have begun processing synthetic or other opportunity crudes and the process of making synthetic crude often involves a coking step. In addition, it is becoming more common to use silicon additives in the drilling process, and for pipeline companies to use them for both flows enhancing performance and foaming issues. It has also been found that silicon additives are sometimes used in barge unloading.

In the hydrotreater, the silica fragments from the antifoam agent undergo a condensation reaction with the alumina surface of the catalyst forming a strong chemical bond. Once the silicon is bound to the alumina surface, it cannot be removed by regeneration or other means. It is a more moderate poison compared to contaminants like sodium or arsenic, but it nonetheless results in activity loss of the order of 5-10°F (3-6°C) for each 1.0 wt% Si deposited on the hydrotreating catalyst.

A variety of analytical techniques have been applied to silicon poisoned catalysts, and this confirms that the silicon is associated with the alumina support as opposed to the active metal sulfides of the catalyst. Furthermore, the silicon is dispersed throughout the available alumina surface as opposed to poisoning only the exterior of the catalyst pellet. As a consequence, the available alumina surface area of a catalyst has a significant impact on silicon capacity of a catalyst.

Another important aspect of silicon poisoning is that silicon pickup depends on unit operating temperature. Commercial data clearly show that the operating temperature of the application must be considered when discussing silicon pickup capacity and when designing effective guard catalyst systems. The maximum capacity of the catalyst needs to be considered as well as the capacity at the operating temperatures of the specific unit in order to accurately predict the point at which silicon will breakthrough into the next bed of catalyst or refinery unit.

Accurately measuring silicon in naphtha streams can be done but it takes a bit of work to get a representative sample of the naphtha. The silicon in the coker naphtha depends on the type and amount of antifoam chemical at the delayer coker unit. Delayed cokers have cycles ranging anywhere between 8 – 24 hours. The coker unit is continually producing a coker naphtha stream during these cycles which is typically being sent from the fractionator straight into the naphtha hydrotreater feed drum. The antifoam chemical is usually not added for the entire coker cycle. This means that the silicon in the naphtha stream will vary with the timing of the coker cycle. In order to get a representative amount of silicon in the coker naphtha stream a composite should be made of hourly samples mixed together for the time of the cycle. For example, for an eight hour cycle eight samples would be mixed and the composite sample analyzed for silicon. To measure the silicon an ICP-MS (Inductively Coupled Plasma Mass Spectrometry) instrument can be used. This instrument/method can measure very low metal concentrations.

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2014
