

# The Science of Sulfidation

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The chemical understanding of how these chemicals like DMS function as sulfidation agents is still an active area of research. This is surprising in light of how long industrial steamcracking operations have used sulfidation agents to manage olefin production – in excess of 50 years.

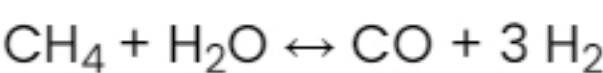
During our history as a DMS supplier to the the ethylene industry, Gaylord Chemical has had relationships with furnace engineers, OEM technologists, industry consultants and others knowledgeable in the field. We’ve worked to gain a basic understanding of the science behind the furnace sulfidation phenomenon. Below are summaries on key subjects.

## The Actual Purpose of Sulfidation Agents

Furnace Engineers have indicated firmly in some cases that DMS is required to control coking rates, thus extending furnace run length between decoking operations. In other cases, ethylene engineers have told Gaylord that the more important purpose of the sulfidation agent is to mitigate carbon monoxide (CO) levels in the furnace effluent. This may be especially important during startup.

It has been proposed that a relationship exists between CO levels and coke formation. This theory holds that CO is produced by the thermal oxidation of coke which has been deposited in the furnace. As such, CO regulation would be largely dependent on the control of coking rates.

Froment (1) proposes that CO formation is independent of coke formation. He attributes CO formation to a version of the steam reforming reaction used for the industrial production of CO / CO<sub>2</sub>:



The industrial CO / CO<sub>2</sub> process relies on Ni catalysis; Ni sites are available in the steamcracking process as Ni is an alloy component of the cracking coil. Reniers and Froment (2) report an asymptotic rate of CO generation which can be explained in terms of the decreasing availability of catalytic sites with time as coke fouling precludes access by hydrocarbon and steam during the run. This is consistent with industrial observations related to Gaylord by ethylene engineers: CO generation is at its highest early in the run when the decoked tube surface provides the highest degree of exposure to catalytic sites.

Sulfur compounds are potent poisons for Ni catalysts and it seems plausible that DMS (or DMS decomposition byproducts) function to control CO generation in this manner. Interestingly, there is good experimental evidence (3) that shows that metal components from the tube wall are present in the coke filaments that develop over time. Thus a sulfidation agent has a continued – if perhaps lessened- role to play in controlling CO rates even after much of the coil surface has been fouled by coke deposits.

The role that sulfidation agents play in controlling coking rates is harder to understand. Careful studies by workers at the University of Ghent (2) suggest that sulfur chemicals may actually *accelerate* coking rates. They further found that a relationship between the thermal stability of the sulfidation agent and an undesired increase in coking may exist. Dimethyl Disulfide (DMDS) is the least thermally stable of the common sulfidation agents and caused dramatically enhanced coking rates compared to the other tested thiochemicals.

As discussed below, there are several mechanisms which can be invoked to explain furnace coking, and the above observation may be attributable to the negative effect that DMDS may have on the heterogeneous noncatalytic coke formation mechanism, wherein free radicals formed by the sulfur chemical propagate to the surface of the coke filaments, forming a macroradical which can grow via interaction with unsaturated compounds in the gas phase (ethylene, propylene, etc.).

In one case it was related that rapid coking ensued in an industrial ethylene furnace after sulfur chemical injection was discontinued. This was explained as being the result of transfer line exchanger (TLE) fouling and was perhaps not due to coking in the cracking coil. The TLE operating conditions and metallurgy are such that a different coking mechanism (Heterogeneous catalytic coking) may be operative; when sulfur injection ceased the previously passivated TLE surface coked quickly. In practice it is apparently difficult to ascertain the point at which coking results as the indicator is an overall change in pressure drop.

The potential for different coking mechanisms to be at play makes it more complicated to understand the role that sulfidation agents play in this aspect of ethylene production. A perception which is held by many engineers is that the sulfur agent passivates the coil surface, thereby inhibiting the formation / decomposition of metal-hydrocarbon complexes. The resulting carbonaceous deposits are a source of coke (4). While industrial experience holds that sulfur agents play a role in coke regulation in the ethylene process, there is a not a clear understanding of how this might occur. There is some pilot scale evidence to suggest that sulfur agents exacerbate the problem of coke formation; this phenomena is difficult to study at industrial scale.

## The Mechanism of Coke Formation

There are several explanations which attempt to describe the formation of coke in the industrial steamcracking process.

*Heterogenous catalytic coke formation* starts on the coil wall and involves 1) the initial chemisorption of hydrocarbons 2) transformation of the resulting metal / hydrocarbon complex into carbonaceous deposits on the coil wall 3) and the growth of carbon filaments from the deposits which develop on the coil surface.

It is a widely held belief that sulfur agents serve to inhibit coke formation produced in this way by passivating catalytic metal sites in the coil wall. Interestingly it has been difficult for researchers to validate this experimentally; one study (3) found no significant difference between coking rates with / without presulfidation – an an *accelerated* coking rate when the sulfur agent is injected.

*Heterogeneous non-catalytic coking* is thought to occur as coke further develops on the growing coke filaments. This mechanism is invoked to explain the experimental observation that sulfur agents can accelerate coking rates. Decomposition of the sulfidation agent into free radical species initiates polymerization between unsaturated species (ethylene, propylene, etc.) and the filament macroradical. As previously mentioned, less thermally stable sulfur compounds appear to generate coke at a faster rate, with DMDS producing the worst asymptotic coking rate among the sulfur agents tested (2). Winker (5) discussed the ability of sulfur (thiophenyl) radicals to react with coke.

*Homogeneous gas phase coking* involves the formation of heavier hydrocarbon species *vi*agas-phase free radical reaction. This mechanism may be important when heavy feedstocks are cracked, and negligible under cracking conditions with common feeds. The rate of this reaction is limited by the low partial pressure of hydrocarbons in the furnace during cracking, one of the principle roles of dilution steam.

## The Mechanism of CO Formation

A persuasive case has been made that CO formation in an ethylene furnace is analogous to the industrial steam reforming process. There is good lab-scale evidence that suggests that dosage of sulfidation agents drastically reduces CO yield under representative cracking conditions (3,6). Sulfur injection apparently serves to poison the catalytic function of Ni / Fe sites on the tube wall or in coke microfilaments, decreasing the potential for CO formation.

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(5) Winkler, J.K.; Karow, W. Rademacher, P. Journal of Analytical and Applied Pyrolysis 62 (2002) 123-41.

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