# REACH – SULFIDATION & SPIKING SUMMARY

SULFIDATION

Organosulfur chemicals are the preferred reagents for catalyst sulfidation. These compounds improve initial catalyst activity and lengthen production cycles for NiMo, CoMo, NiW and CoW hydrotreating catalysts. It is the H2S formed when the chemical reaction between DMDS and H2 occurs that is responsible for the conversion of the metal in the catalyst from the oxide state to the sulphided state. This latter state is the active form.

Many Sulphur compounds can be used (EM, TBM, DMS, TNPS 537, TBPS 454) but today DMDS is the most popular choice.
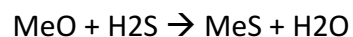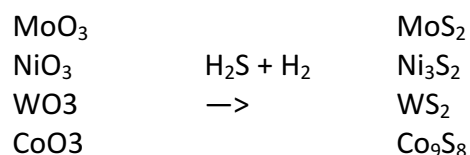
The general reaction chemistry is:

R-S-R + H2 → H2S + 2 R-H

Therefore for DMDS we have:
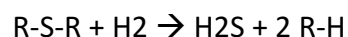
CH3-S-S-CH3   +   3H2   →   2H2S   +   2CH4 (methane)

Then the conversion of the metal in the catalyst to the metal oxide (active) form in the catalyst:

MeO + H2S → MeS + H2O

Typically:

MoO_3		MoS_2
NiO_3	$H_2S + H_2$	Ni_3S_2
WO3	—>	WS_2
CoO3		Co_9S_8

Metal	Oxide	Sulfide	H_2S required/mole metal
Mo	MoO_3	MoS_2	2 mole
96	96+(3x16)=144	96+(2x32)=160	2x{(2x1)+32)}=68
W	WO_3	WS_2	2 mole
184	184+(3x16)=232	184+(2x32)=248	2x{(2x1)+32)}=68
Ni	NiO_3	Ni_3S_2	2/3mole
59	59+(3x16)=107	1/3x{(3x59)+(2x32)}=80.3	2/3x{(2x1)+32)}=22.7
Co	CoO	Co_9S_8	8/9mole
59	59+16=75	1/9x{(9x59)+(8x32)}=87.4	8/9x{(2x1)+32)}=30.2

* atomic masses to nearest whole number

i.e. 96 (g/kg/lb) Mo equivalent to 144 (g./kg./lb.)oxide forms 160 (g./kg./lb.)
 sulfide which requires 68 (g/kg/lb) H$_2$S
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Exotherms from sulfiding Chemicals- Co/Mo Catalyst , 28 bars Hydrogen
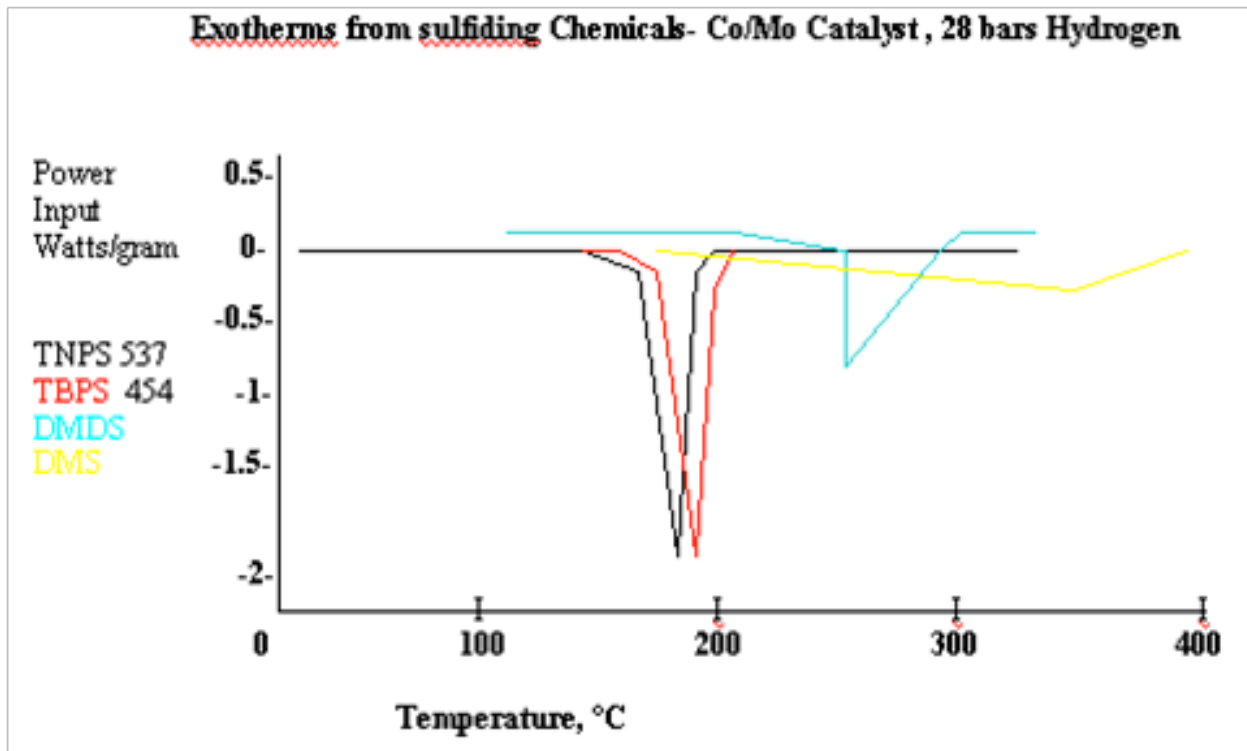
SPIKING

The manufacture of olefins such as ethylene, propylene and higher types by thermal cracking of hydrocarbons in presence of dilution steam in tubular reactors and its economics are greatly affected by undesired side reactions. These side reactions, among which are coke and CO formation, reduce the olefins yield and limit equipment performance. Tube metallurgy and operating conditions severity are known to influence both CO and coke. A variety of chemicals are added to feedstock or dilution steam streams to help control coke and CO formation.

Many Sulphur compounds can be used (EM, TBM, DMS, TNPS 537, TBPS 454) but today DMDS is the most popular choice.
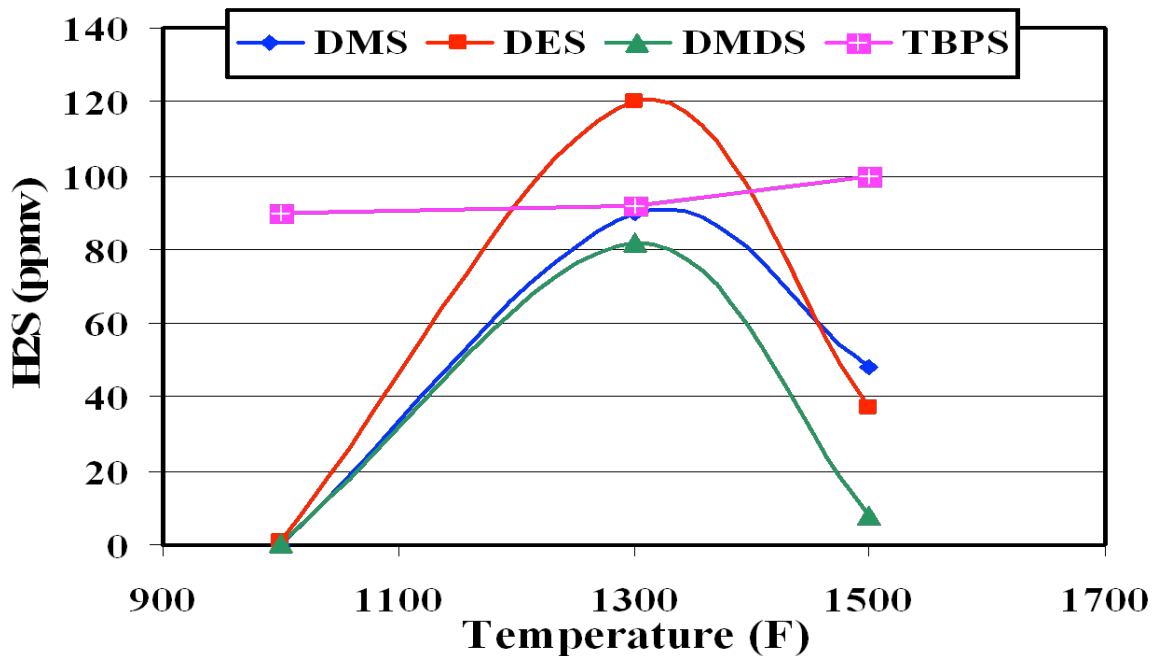
The chemistry is the same as for Sulfidation:

R-S-R + H2 → H2S + 2 R-H

Therefore, for DMDS we have:
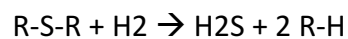
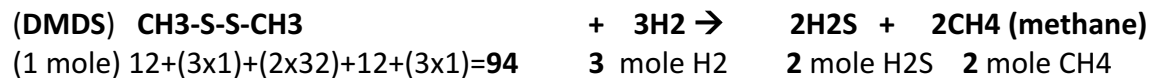**CH3-S-S-CH3   +   3H2 →   2H2S +   2CH4 (methane)**

The sulphur from the H2S is used to protect the metallurgy and help inhibit the formation of coke.

GENERAL INFORMATION FOR SULFIDATION AND SPIKING

If the reaction of DMDS in a hydrogen rich environment were to give 100% theoretical yield of H2S and methane, the stoichiometry is as follows:

(DMDS) CH3-S-S-CH3   **+   3H2 →   2H2S +   2CH4 (methane)**
(1 mole) 12+(3x1)+(2x32)+12+(3x1)=**94**   **3** mole H2   **2** mole H2S   **2** mole CH4

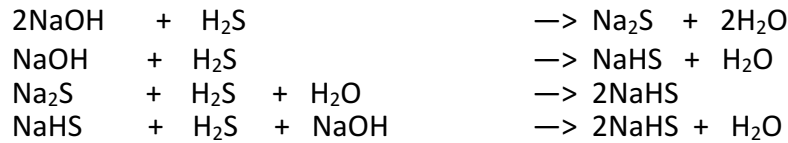S content DMDS is (2x32)/**94**x100=68% ; **94/2** or 47 g. required per mole of H2S
3/2 or 1.5 mole H2 required per mole of H2S
2/2 or 1.0 mole hydrocarbon (methane) produced per mole H2S

Then 42.72 kgs of DMDS would give 14.54 kgs of CH4 and 30.90 kgs of H2S.

Various methods may be used for the disposal of spent caustic including incineration; sending to a flare from a wet oxidation process or, using a biochemical process. This will depend on the designer of the unit. For example, if this is ADNOC then this is an ethane cracker designed by Linde, so H_2S is almost completely removed in the caustic tower and final disposal is by a spent caustic handling system.
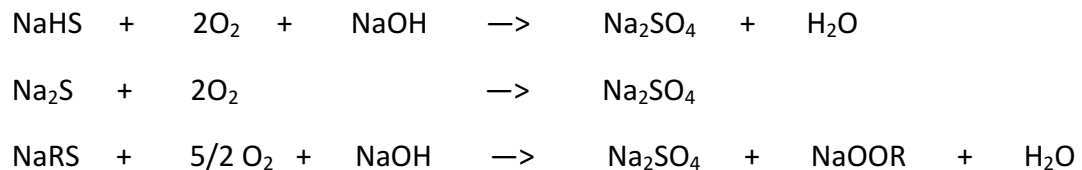
The possible reactions in a caustic tower are:

$$2NaOH \quad + \quad H_2S \qquad\qquad\qquad —> Na_2S \ + \ 2H_2O$$
$$NaOH \quad + \quad H_2S \qquad\qquad\qquad —> NaHS \ + \ H_2O$$
$$Na_2S \quad + \quad H_2S \ + \ H_2O \qquad —> 2NaHS$$
$$NaHS \quad + \quad H_2S \ + \ NaOH \qquad —> 2NaHS \ + \ H_2O$$

The resulting spent caustic typical composition is:

Composition	Wt %
Na_2CO_3	1 - 8
Na_2S/NaHS	0 - 3.5
NaOH	1.5 - 2.5
NaRS	0.0 - 0.2
NaCl	0.0 - 0.05
Dissolved H/C	0.0 - 0.04
Phenol	0.0 - 0.025
Cyanides	0.0 - 0.05
H2O	Balance

If incineration is used for spent caustic disposal, the fate of the H_2S depends on the temperature of incineration. In USA it is not possible to incinerate as it is required to have more than 98% destruction. The preferred method of disposal of the spent caustic is wet oxidation. Sulfides must be converted by oxidation to sulfates or thiosulfate or by neutralization to hydrogen sulfide gas, which may be sent to a sulfur recovery plant, be reused or be burned in the flare.

If oxidation is used in the spent caustic handling process, then

$$NaHS \quad + \quad 2O_2 \quad + \quad NaOH \quad —> \quad Na_2SO_4 \quad + \quad H_2O$$

$$Na_2S \quad + \quad 2O_2 \qquad\qquad\qquad —> \quad Na_2SO_4$$

$$NaRS \quad + \quad 5/2\,O_2 \ + \ NaOH \quad —> \quad Na_2SO_4 \quad + \quad NaOOR \quad + \quad H_2O$$

There is always a small amount of H_2S generated and sent to the flare. Spent caustic wet air oxidation units operated at relatively high temperatures (greater than 240°C (or °F)) will oxidize more of the organics present in the feed. Usually organic oxidation results in breaking large molecules into smaller ones. Except for wet air oxidation units that run at extreme oxidizing conditions, most of the organics end up as simple acids (acetic acid, formic acid, etc.) or their basic counterparts (acetate, formate). The net effect of wet air oxidation is a reduction in alkalinity and COD. All CPC's plants in the USA and Middle East all have a Zimpro wet oxidation system.

From CPChem's point of view, the chemical processing that takes place is the transformation of DMDS into H2S. Therefore, DMDS is regarded as an intermediate in the manufacture of H2S. This is in line with the REACH Regulation Article 3(15) and also with the Guidance Document on Intermediates version 2.0 dated December 2010. The substance H2S formed from DMDS will further react with the metals of the catalyst and any residuals of H2S will be treated as a waste.