DRAFT

AGENT of change

FRANCIS HUMBLOT, ARKEMA, FRANCE, EXAMINES THE CHOICE OF SULFIDING AGENTS FOR HYDROTREATING CATALYSTS.

Hydroprocessing operations such as hydrodesulfurisation, hydrotreating, hydrocracking or atmospheric residue desulfurisation are of increasing importance. Drastic regulations on distillates first targeted the reduction of sulfur emissions. Now the ultra low sulfur distillates must comply with DeNOx catalytic pot request and are already the standard in many countries.

Improvement in catalyst performance has been one of the keys to producing ultra low sulfur diesel (ULSD). Generally, commercial hydrotreating catalysts are based on molybdenum or tungsten in combination with a promoting metal such as nickel or cobalt. CoMo, NiMo or NiW species in their oxide forms are supported on alumina or on zeolite carriers. They have to be sulfided in order to reach their active forms. This sulfiding operation is critical, as the formed transition metal sulfides are carrying the active sites responsible for the catalyst performance. The good and safe formation of the transition metal sulfide phase has a direct impact on the activity and on the run length of the hydroprocessing unit.

Once the refiner has selected a suitable catalyst oxide, an important aspect in having optimal catalyst efficiency in a hydrotreater is to select the best sulfiding agent. Arkema produces a large variety of compounds such as sulfides, disulfides, polysulfides and mercaptans. The aim of this article is to explain that the selection of the most suitable sulfiding agent is based on physical and chemical properties necessary for the catalyst activation.

Table 1. Physical properties of some commercial organo sulfur compounds

	DMDS	DMS	TNPS	TPS54	NBM	EM
Name	Dimethyl disulfide	Dimethyl sulfide	Ternonyl polysulfide	Terbutyl polysulfide	n-butyl mercaptan	Ethyl mercaptan
Molecular weight (g mol^{-1})	94.2	62.1	414*	248*	98	35
Boiling point (˚C)	109.6	37	160	170**	98	35
% sulfur	68	52	36	54	36	52
Density	1.063	0.843	1.05	1.082	0.834	0.830
Sulfur content (g/l)	720	440	380	584	300	430
Vapour pressure at 20 ˚C (mbar)	29.3	505	0.03	<0.1	48	535
Viscosity at 20 ˚C (cPs)	0.62	0.28	184	12.8	0.5	0.23

** Average molecular weight. ** Start of thermal decomposition at 170 ℃*

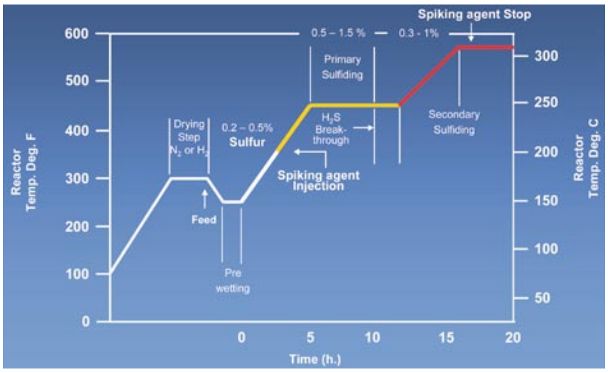

Figure 1. Dimethyl disulfide conversion on CoMo/alumina catalyst and hydrogen (1 bar).

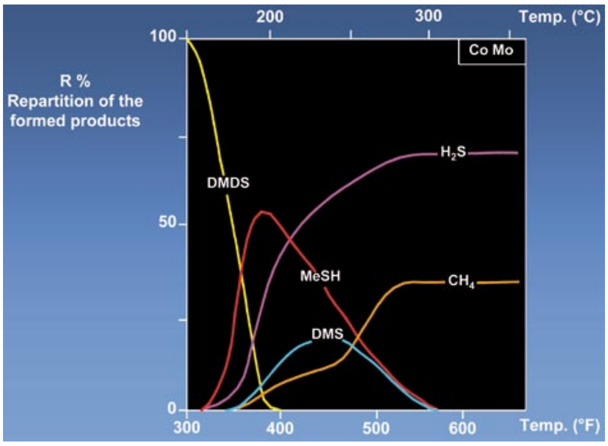

Figure 2. Dimethyl disulfide reaction with hydrogen (1 bar) in the presence of CoMo/alumina catalyst, effect of temperature.

Chemistry of catalyst sulfiding

A sulfiding operation involves a sulfiding agent and a reducing agent to transform transition metal oxide species into a metallic sulfide crystalline phase. With a sulfiding agent such as dimethyl disulfide (DMDS) and the most common metal oxides used for hydrotreating catalysts, these reactions are:

$$MoO_3 + CH_3\text{-}S\text{-}S\text{-}CH_3 + 4H_2 \rightarrow MoS_2 + 2CH_4 + 3H_2O$$
$$\Delta H = -77.52 \text{ kcal/mol of } MoO_3$$

$$3NiO + CH_3\text{-}S\text{-}S\text{-}CH_3 + 4H_2 \rightarrow Ni_3S_2 + 3H_2O + 2CH_4$$
$$\Delta H = -30.2 \text{ kcal/mol of } NiO$$

$$9CoO + 4CH_3\text{-}S\text{-}S\text{-}CH_3 + 13\,H_2 \rightarrow Co_9S_8 + 9H_2O + 8CH_4$$
$$\Delta H = -17.5 \text{ kcal/mol of } CoO$$

The conversion of Mo, Co and Ni oxides are exothermal reactions with hydrogen sulfide or dimethyl disulfide. This is why the activation of a hydrotreating catalyst has to be kept under control to avoid a large exotherm. Moreover, the formed metal sulfide crystals, their size, their size distribution and their interaction with the carrier are important parameters for the activity of active sites. The sulfiding procedure has been optimised by catalyst vendors to create the best catalyst structure and obtain high and stable activity. For all these reasons, the sulfiding operation has to be performed carefully and is critical for hydrotreating unit performance.

Sulfiding procedures have been designed to avoid undesirable side reactions such as:

- Partial or total reduction of metal oxides. The sulfiding reaction involves a decrease of oxidation number such as $Mo^{VI}O_3$ to $Mo^{IV}S_2$. This partial reduction is performed with one molecule of hydrogen. However, the first reaction of MoO_3 should be a partial sulfiding to MoO_xS_y. If this reduction happens before sulfiding, MoO_2 or Mo metal can be formed. These reduced species are kinetically more difficult to sulfide and finally a lower catalyst activity is obtained. This undesirable reaction is inhibited in the presence of an active sulfiding agent which preferably reacts with oxide species before their hydrogen reduction.
- Deposition of coke. A more classical deactivation process, coke deposition is enhanced by high temperature (exotherms) and poor hydrogen coverage (low hydrogen purity or pressure). During the catalyst activation process, the sulfiding agent flow rate is adjusted to avoid having an exotherm that is too large and the purity is kept above 60% by injecting fresh hydrogen.

Physical properties of commercial organo-sulfur compounds

Arkema produces a wide range of sulfiding compounds. From among mercaptans, sulfides, disulfides and polysulfides, DMDS has properties well suited to the sulfiding application (Table 1). DMDS has the highest content of sulfur (68%) minimising the quantity of organo-sulfur to handle and store on site. Its low vapour pressure is a safety factor in the event of leakage by limiting the evaporation.

Chemistry of sulfiding agents

Three different possibilities can be seriously considered to sulfide a hydrotreating catalyst:

- DMDS.
- Sulfur coming from the sour feed.
- Terbutylpolysulfide (TPS54).

Figure 1 shows a typical inlet catalyst temperature profile for spike feed sulfiding (DMDS or TPS54).

- 180 - 230/240 ˚C, primary sulfiding: sulfur compounds react with the catalyst to partially sulfide the metallic oxides. In order to avoid any reduction of the catalyst, the inlet temperature is maintained at 230 - 240 ˚C and it is generally recommended not to exceed 15 - 20 ˚C of temperature difference between the inlet and the outlet of the catalyst bed. This exotherm generated by catalyst sulfiding is kept under control by limiting the sulfur amount carried by the spiking agent to a maximum of 1%. When the catalyst starts to be saturated with sulfur at this low temperature, hydrogen sulfide formed from organo-sulfur hydrogenolysis does not react anymore with the catalyst and escapes from the outlet of the reactor. As soon as the H_2S concentration in hydrogen goes above 3000 - 5000 ppm ('H_2S breakthrough'), the catalytic reactor can be heated to a temperature above 300 ˚C without any reduction risk for the catalyst. Generally, the H_2S breakthrough is obtained at around 50% of the sulfur stoechiometry.
- 230/240 - 320/350 ˚C, secondary sulfiding: This high temperature sulfiding is required to finish the conversion of remaining oxides into active metallic sulfides. It is actually in this second stage of the reaction that the final catalyst structure is obtained. The missing 50% sulfur stoechiometry is injected during this period at a dosing rate adjusted to maintain a H_2S concentration in hydrogen between 1 - 2%. At that stage, it is important to always maintain more than 0.3 - 0.5% of H_2S to avoid any catalyst reduction and catalyst activity lost.

DMDS

Figure 2 shows the conversion of DMDS with hydrogen (normal pressure) and in the presence of a CoMo (cobalt plus molybdenum) catalyst. Since the oxide catalyst reacts with the injection of DMDS even at a low temperature, it is necessary to wait several hours to stabilise the DMDS conversion and the outlet composition. This experiment was repeated at different temperatures, as shown in Figure 2.

DMDS is known to be thermally stable up to 300 ˚C with hydrogen but, because of the presence of metallic oxides such as MoO_3, DMDS starts to decompose at a much lower temperature (50% conversion at 170 - 180 ˚C). Above 200 ˚C, DMDS is totally converted. The primary product is methyl mercaptan, corresponding to the sulfur-sulfur bond hydrogenolysis, rapidly followed by the formation of both hydrogen sulfide and dimethyl sulfide (DMS), formed by the combination of the molecules of methyl mercaptan. At 230 - 240 ˚C (the temperature generally used for primary sulfiding), hydrogen sulfide is the main decomposition product of DMDS. Hydrogen sulfide reacts rapidly with the catalyst, which becomes more active and also converts methyl mercaptan and dimethyl sulfide more and more easily. Above 270 - 300 ˚C, the sulfiding species is only H_2S.

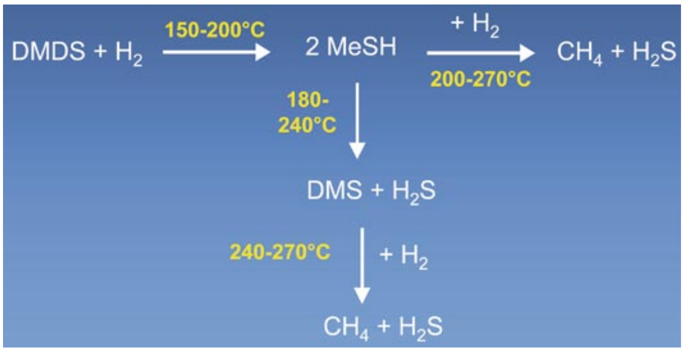

Figure 3. Reactions of dimethyl disulfide reaction with hydrogen (1 bar) in the presence of a CoMo/alumina catalyst.

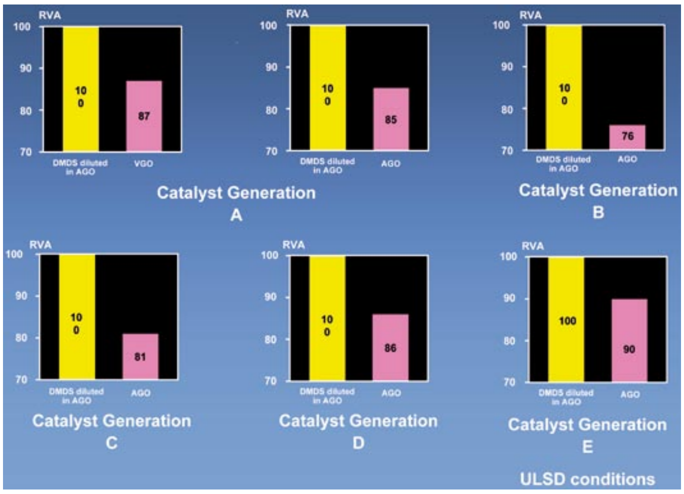

Figure 4. Activity of different generation catalysts sulfided by DMDS (relative volume activity = 100) or by sour feed.

At any temperature, the only hydrocarbon formed is methane, which is known not to be a coke precursor on the catalyst. The DMDS chemistry in contact with a hydrotreating catalyst and hydrogen is summarised in Figure 3.

Sour feedstock

The target of catalyst sulfiding is to form active species with the highest activity. Figure 4 shows the impact of the sulfiding agent on catalyst activity. The activity of DMDS sulfided catalysts is compared to the activity of the same catalyst sulfided with a sour feedstock containing 0.8 - 1.2% of sulfur. Activity tests of Generation A-D catalysts have been performed on a pilot in the refining Total's research centre at Solaize (France). Recently, these results were completed at CPERI in Greece by activity tests performed on the latest generation CoMo catalyst (generation E) under ultra low sulfur desulfurisation (ULSD) conditions. All these activity tests performed on five different catalyst generations show that DMDS sulfiding leads to the highest initial activity.

This result is linked to the nature of the organo-sulfur compounds. In the case of sour feedstock sulfiding, the organo-sulfurs contained in the feedstock belong to thiophene, benzothiophene, dibenzothiophene and their substituted homologues. These compounds are refractory to release their sulfur and therefore need higher temperature for primary sulfiding (270 ˚C instead of 230 ˚C for DMDS). Moreover, real feedstock sulfiding needs a longer time, typically double, to obtain the hydrogen sulfide breakthrough and the sulfur stoechiometry on the catalyst. These severe conditions are more risky for the catalyst and can promote its reduction or coke deposition.

Furthermore, sour feed sulfiding needs the preparation and storage of a large sour feed volume and the temporary storage of the feed out of specification which is exiting the reactor during the sulfiding operation. All these constraints are avoided by using DMDS.

Polysulfides: TPS54

The chemistry of polysulfides is different compared to the DMDS chemistry. Polysulfides and particularly TPS54 are known to be unstable with temperature. Figure 5 shows the thermal decomposition of TPS54, which happens in the preheating section before reaching the catalyst bed.

During sulfiding at intermediate temperatures, polysulfides form isobutylene, which is a coke precursor. Moreover, polysulfide conversion at intermediate temperatures in the presence or absence of a catalyst leads to elemental sulfur formation. Solid deposit by using polysulfides can result from this elemental sulfur precipitation at intermediate temperature or from carbon-sulfur (Carsul) formation. Carsul is a polymeric product resulting from the recombination of elemental sulfur with olefins (Figure 5) capable of plugging pipes, increasing the pressure drop in a catalyst bed or hindering access to active sites.

Due to the different chemistry of TPS54, its usage for catalyst sulfiding is restricted and more risky overall. Since sulfur deposition happens at low temperature without reaction on the catalyst, the excess of TPS54 must be avoided below 250 ˚C because of the risk of accumulation and of local exotherms. Moreover, the injection point has to be close to the catalyst bed in order to avoid solid deposition in the preheating section because of the Carsul formation. This injection point is generally at high pressure and is not as convenient compared to injection at the suction on the feedstock pump. Finally, it is impossible to perform gas phase sulfiding (sulfiding without feedstock or light feedstock such as naphtha totally vaporised during catalyst activation) since any solid formation will create local plugging and a pressure drop increase.

Because of the differences between the chemistry of polysulfides and DMDS, Arkema recommends DMDS sulfiding as the safest activation procedure without any risk of sulfur deposit in the vessel.

DMDS-Evolution

DMDS-Evolution (DMDS-E) was launched in 1999 by Arkema. It was the result of extensive R&D investment aimed at addressing the odour issue for all applications and activity performance for hydrotreating catalyst sulfiding.

First and foremost, a drastic reduction in volatiles (particularly methyl mercaptan) has been obtained by implementing a purification step in the industrial DMDS production process to moderate the odour. Since then, methyl mercaptan has been a specification of DMDS-E with a maximum concentration of 0.01%, which ensures a much less aggressive odour. Furthermore, the slight blending with a selection of organic additives changes the residual odour to make it more user friendly.

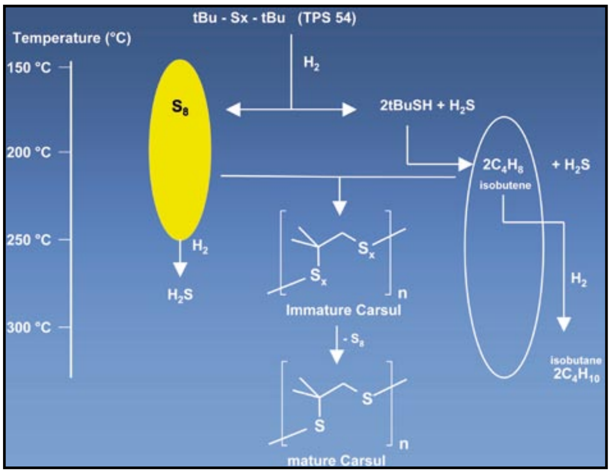

Figure 5. Thermal decomposition of terbutyl polysulfide (TPS54) in the presence of hydrogen.

DMDS-E has the same physical and chemical properties of DMDS. The continuous manufacturing process ensures a very stable and high quality product without any contaminants such as heavy metals, sodium or nitrogen.

Activity tests with DMDS-E were performed in 1999 at Total's Solaize research centre to validate this new product for catalyst sulfiding. These tests showed an activity increase of 10 - 15% compared to standard DMDS, explained by the presence of the organic additives inside DMDS and their interaction with the catalyst during the sulfiding reaction. For this reason, DMDS-E is particularly recommended for hydroprocessing catalysts sulfiding. Since 1999, this new DMDS quality has been a success in hydrotreating catalyst sulfiding. More than 80% of Arkema's customers are now using this new grade.

Conclusion

Organo-sulfur compounds such as mercaptans and sulfides are widely used as sulfur donors in a number of reactions in the chemical, petrochemical and refining industries. On the basis of its specific physical and chemical properties, DMDS is frequently utilised as a catalyst sulfiding agent in refineries.

Converted in the presence of H_2 at low temperatures on CoMo, NiMo and NiW catalysts, DMDS ensures a safe catalyst sulfiding and maximised catalyst activity. It has low volatility and therefore presents a limited environmental risk. With its high sulfur content and density, DMDS is an ideal sulfiding agent for refining applications.

As a leading DMDS manufacturer, Arkema guarantees a reliable supply worldwide based on a network of bulk storages (Europe, America, Asia and the Middle East) and a large fleet of dedicated containers. Arkema's product of choice is DMDS-Evolution® (DMDS-E), developed after extensive research to address the odour issue in all applications, as well as activity performance in hydrotreating catalyst sulfiding. As DMDS-Evolution® and conventional DMDS share the same physical and chemical properties, DMDS-E is used in the same way for all applications, including hydrotreating catalyst sulfiding.