

EUROPEAN CATALYST MANUFACTURERS ASSOCIATION (ECMA)

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REACH AND CATALYSTS (FRESH AND SPENT) **A position paper by the European Catalyst Manufacturers Association (ECMA)**

Catalyst use involves complex interactions within the reactor, sometimes creating new chemical substances during their life cycle which may have regulatory implications under REACH and/or waste regulations. In order to better define what some of these regulatory obligations may be, the European Catalyst Manufacturers Association (ECMA) is hereby preparing this document as a reference to help catalyst users assess their particular manufacturing process with respect to these regulations. It is implicit that each catalyst user has a unique obligation to examine each of their catalyst processes to determine what, if any substances may be formed in the reactor on or in the catalyst, if they remain in the process streams leaving the reactor and are subsequently isolated, or if they remain in the reactor and are subsequently discharged with the spent catalyst. The catalyst itself is another potential source of new substances with potential regulatory impact.

All the steps presented below are summarized for an example HDT Catalyst in the Overview Diagram on the last page.

From REACH perspective:

1. Fresh catalysts

Most catalysts are generally considered to be “mixtures”, consisting of a number of chemical substances. The individual substances in fresh catalysts must be pre-registered and registered under REACH by the catalyst manufacturer/importer (M/I) or only representative (OR). Depending on the assessment of the M/I/OR, some catalyst components (substances) may be considered by the M/I/OR as being “transported isolated intermediates” (Art.18.4.).

2. Activated catalysts

Most catalysts must be activated before use. This involves chemical reactions, creating new chemical substances that are considered to be “manufactured” under REACH and that must be pre-registered and registered by the facility at which these reactions occur if they do not meet the definition of non-isolated intermediates [NOTE: there could be exceptions to this – see discussion of Spent Catalysts below]. As an example, for hydrotreating catalysts, this means the metal oxides in the fresh catalyst must be reduced, usually by introducing sulfur to convert the metal oxides into metal sulfides.

- a. If this activation occurs in the reactor at the customer’s site (in-situ), the metal sulfides formed are considered to be “manufactured” by the customer and the assessment of these substances will most certainly lead to a characterization of them as non-isolated intermediates, thus exempt from REACH (Art.2.1 (c)). The next step in the assessment will be “spent catalyst” (see below).
- b. If this activation occurs before the catalyst is delivered to the customer (ex-situ) in a process called “pre-sulfiding”, the metal sulfides are considered to be “manufactured” by the facility that performs this process and that facility must pre-register and register the metal sulfides under REACH.

3. Spent Catalysts

Spent catalysts are "manufactured" at the refineries or chemical plants. The physical properties of spent catalysts as well as their composition are generally different from the fresh catalysts (for example, spent refinery hydrotreating catalysts are typically self-heating, contain metal sulfides and coke and may have additional substances (contaminants; could possibly be considered as by products) deposited during service that were not present in the fresh catalyst...some of which may contribute to the hazards of the product [for example vanadium, arsenic and iron].

The spent catalyst is either treated in the reactor such that the metal sulfides are converted back to the metal oxides before the spent catalyst is discharged, or discharged from the reactor while still containing metal sulfides. In both cases either:

a. If the spent catalyst owner intends to consign the material into a recycling or disposal operation, it will automatically be defined as waste under Directive 2008/98/EC (Art.3 (1)) and thus be exempt from REACH, but must conform to all aspects of waste legislation.

-OR-

b. However, if the spent catalyst is being sent off the originating site for regeneration and the ownership of the catalyst does not change, then some national authorities may consider the material as a product rather than a waste. The catalyst user should check with their local competent authority to confirm situations where this will apply.

In the case of treatment before discharge, since the metal oxides have already been pre-registered and registered up the supply chain by the catalyst manufacturer under REACH, the catalyst owner, i.e. Downstream User (DU), does not have any obligation to register them.

If discharged while still containing metal sulfides, the catalyst owner (refinery or chemical plant), as the “manufacturer” of the spent catalyst, would be the party to pre-register and register the substances formed in the reactor. The metal sulfides previously considered as non-isolated intermediates (see Activated Catalysts), could be considered as transported isolated intermediates (Art.18.4.).

However, the additional components deposited on the catalyst during service still have to be considered under REACH. Until these components are discharged from the reactor they are non-isolated intermediates and are exempt from REACH (Art 2.1 (c)). Once discharged, petroleum coke is specifically exempted from registration and evaluation (Art. 2.7(b) Annex V.10). The other contaminants (examples include vanadium, arsenic and iron) could be considered as by-products, and if so, are exempted from registration and evaluation obligations under REACH (exempted under: Art 2.7(b) Annex V.5).

Although these deposited substances may be exempted from REACH pre-registration and registration requirements, their hazards still must be considered and included in any hazard communication documents prepared for the spent catalyst (such as Material Safety Data Sheets and labels). Thus they may contribute to the hazards and classification of the spent catalyst.

For the specific case of FCC catalyst, and depending on the IED permit of their cracker unit, the spent catalyst owner may even specify regenerated spent catalyst as waste. Here the classification of the EU waste framework directive and the national requirements need to be carefully considered. The IED directive only distinguishes between products and waste; therefore a reclassification may have also an impact on the operational permit of the unit.

4. Regeneration of Spent Catalysts

When spent catalysts are regenerated, the site that does the regeneration is considered to "manufacture" the regenerated catalyst. Thus under REACH, the legal entity doing the regeneration would be required to pre-register and register the metal oxides and any other substances created during the regeneration operation.

For chemical substances that result from the regeneration process which are the same as those in the original fresh catalyst (for example the metal oxides), the regeneration site may be exempted from pre-registering and registering requirements under Art.2.7(d), if the substances were properly registered and if the required information is available to them.

Substances different from those in the original catalyst (e.g. additional substances deposited on the spent catalyst during its service at the refinery or chemical plant [for example vanadium and arsenic]) must be pre-registered and registered by the regeneration site under REACH, unless they can be considered as by-products and thereby exempted (Art 2.7 b Annex V point 5).

5. Metal Reclaim/Recycling

When spent catalyst is subjected to metal reclaim/recycling, the site doing the reclaim operation is considered to "manufacture" the metals that are reclaimed. However, similar to the regeneration activity above, if the substances reclaimed/recycled are the same as the ones that have already been pre-registered and registered the reclaim/recycle site does not have to pre-register or register them under REACH. If the substances reclaimed are different chemical substances, then the reclaim site must pre-register and register them under REACH.

When transporting spent catalyst for metals reclaim/recycling, it will be classified as a waste, and the appropriate EU Waste, OECD and Basel Convention regulations must be followed.

Substances that remain after the reclaim/recycling operation and which are being disposed of as waste would fall outside of REACH and instead fall under applicable waste regulations.

6. Spent FCC Catalyst

Spent FCC catalysts are typically not sent for metals reclaim. They may, however, be used as secondary materials for other applications (cement production as an example). REACH requirements would need to be considered on a case-by-case basis.

IMPORTANT NOTE:

In any case where an exemption for (pre-) registration is claimed for a substance because "already (pre-) registered up the supply chain", the claimer has to be able to justify such a claim and needs to produce the supporting documentation (e.g. volumes, substance identity, etc.) for this claim. This will be most likely a case-by-case process involving the whole supply chain up to the (pre-) registrant.

ANNEX 1. Additional Guidance for On-Site Activation of Hydrotreating Catalysts

ECMA has received feedback from catalyst customers requesting that we provide additional guidance regarding likely substances that may be formed when catalysts are activated on-site and which may require pre-registration and registration for REACH by the legal entity where this occurs. We are pleased to provide information on what are thought to be some of the most common substances that may be formed for generic hydrotreating catalysts during the on-site activation process. It must be cautioned that additional or different substances may be formed on individual sites, that there are other types of catalyst and processes that may also form substances with REACH pre-registration and registration implications and that ultimately, it is the responsibility of each legal entity to decide what substances, if any, they will register for REACH. **More specific guidance on a catalyst by catalyst basis may be available from the individual catalyst manufacturers.** The information presented here is NOT the only process that needs to be reviewed and hydrotreating catalysts are only chosen as an example. The guidance presented in earlier parts of this Position Paper still applies and should be used to help decide what should be done for REACH compliance.

With this in mind, the following list represents some (but not all - other activated metal species may also exist) of the most common substances that may be formed when generic hydrotreating catalysts are activated on-site. Additionally, common reference books indicate that the activation reactions of multi-metallic catalysts (NiMo/NiW) produce Trinickel Disulphide, whereas Nickel Sulfide is produced during the activation of mono-metallic catalysts.

<u>Substance</u>	<u>Formula</u>	<u>CAS</u>	<u>EINECS</u>
Nickel sulfide*	NiS	16812-54-7	240-841-2
Trinickel disulfide	Ni ₃ S ₂	12035-72-2	234-829-6
Cobalt sulfide*	CoS	1317-42-6	215-273-3
Molybdenum disulfide*	MoS ₂	1317-33-5	215-263-9
Tungsten disulfide	WS ₂	12138-09-9	235-243-3

* Other CAS/EINECS numbers exist for these substances. These references should normally be included in the same SIEF as those above. For example:

Nickel sulfide (not further specified)	11113-75-0	234-349-7
Cobalt sulfide (not further specified)	12653-56-4	235-751-5
Molybdenum sulfide (not further specified)	12612-50-9	235-721-1

Also, a final reminder that a decision on whether to actually register a substance that has been pre-registered will need to be made prior to the registration deadline for that substance as determined by the volume band for the specific legal entity. It is not required that all substances pre-registered must be registered.

HDT Catalyst Life Cycle : REACH responsibilities

All European actors

