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Life cycle of hydroprocessing catalysts and total catalyst management

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Abstract

Hydroprocessing catalysts based on Ni, Co, Mo and W are used in various refinery processing applications where several deactivation mechanisms become of importance (coke formation, active phase sintering, metals deposition, poisoning) in the catalyst's life cycle. The life cycle of commercial hydroprocessing catalysts is very complex and includes the catalyst production, sulfidation, use, oxidative regeneration followed by re-sulfidation and reuse or, if reuse is not possible, recycling or disposal. To understand the changes in catalyst properties taking place during a life cycle, the catalyst quality in the different stages can be best monitored by using advanced analytical techniques. The catalyst's life cycle is further complicated by numerous technical, environmental and organizational issues involved. In principle, different companies can be involved in each of the life cycle steps. Leading catalyst manufacturers, together with specialized firms, offer refineries a total catalyst management concept, starting with the purchase of the fresh catalyst and ending with its final recycling or disposal. Total catalyst management includes a broad range of services, ensuring optimal timing during the change-out process, reliable, smooth and safe operations, minimal downtime and maximum catalyst and unit performance.

Keywords: Hydroprocessing catalysts; Characterization; (Scanning) transmission electron microscopy-energy dispersive X-ray analysis ((S)TEM-EDX); XPS; Catalyst life cycle

1. Introduction

The oil refining industry is struggling to meet the ever-stricter environmental requirements and product specifications being imposed by government legislation. The main proposed amendments to the European Union Fuel Quality Directives are, from January 1, 2009, the full market penetration of 10 ppm sulfur automotive diesel and a reduction from the current 11 to 8 wt.% for the polyaromatic hydrocarbon content in automotive diesel. Furthermore, from January 1, 2009, the maximum sulfur content in ''off-road'' diesel will be reduced from 1000 to 10 ppm for land-based uses and to 300 ppm for inland waterway vessels. Effectively this means the alignment of off-road diesel fuel with on-road diesel fuel.

Hydroprocessing is one of the most important oil refining processes to address compliance with these regulations. Nearly all crude fractions are currently being subjected to hydroprocessing in some stage of their refining. Hydroprocessing removes various contaminants from the crude oil and results in the finished oil products having improved odor, color and stability characteristics. This makes it possible to meet the strict product specifications, which results in the drastic reduction of emissions of SO_x, NO_x and particulate matter from car engines. In addition to reducing the amount of heavy residue, hydroprocessing also increases the volume of more valuable oil fractions produced, suitable as transportation fuels and raw materials for chemical industry.

Hydroprocessing itself is a process that directly contributes to a cleaner environment. Consequently, also the hydroprocessing catalysts used in this process have to be handled according to the highest environmental standards, since during their life cycle, catalysts are repeatedly being handled and transported by different users and service providers. To improve the safety, timing and economics, an optimized approach is to have a single company to co-ordinate the entire life cycle.

2. Analytical methods

2.1. Sample unloading and storage

The sulfided and used samples were unloaded into a container filled with SRGO and were kept submerged in SRGO in closed

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containers to prevent air oxidation. The samples were further stored and handled in a glove box. Residual SRGO had to be removed from the catalyst particles prior to further analysis. This was done by rinsing the catalyst particles briefly with toluene.

2.2. *Scanning transmission electron microscopy–energy dispersive X-ray [(S)TEM-EDX] analysis*

The samples were powdered, evacuated for at least 2 h at 150 °C and subsequently vacuum impregnated with the standard mixture Ultra Low Viscosity Kit, hard version (Polaron Instruments Inc.). The mixture with catalyst was transferred into a polyethylene capsule (BEEM) and mixed with fresh embedding medium. The epoxy embedding medium was hardened at least 48 h under N_2 (0.2 MPa, 338 K). Sections of about 60 nm thickness were prepared using a Leica Reichert Ultracut-S ultramicrotome, collected on a water surface and transferred to a slightly etched (Ar plasma) Cu grid and dried. The thin sections on the TEM grid were covered with a thin layer of carbon to prevent charging during TEM analysis. Shortly after preparation, the sections were investigated with a JEOL JEM-2010F-HR TEM, with a 200 kV electron beam (Field Emission Gun, FEG), equipped with a STEM unit and a Thermo Noran EDX system. The MoS_2 morphology was studied by TEM imaging under slightly underfocussed conditions (−48 nm). The promoter segregation was studied by STEM-EDX spectral imaging under analytical probe (1.0 nm) conditions.

2.3. *Time of flight secondary ion mass spectroscopy (ToF-SIMS) analysis*

ToF-SIMS analyses have been performed with a ToF.SIMS IV instrument from the manufacturer ION-TOF (Münster, Germany), equipped with a Bi liquid metal primary ion gun. The mass resolution of this instrument is in the range of 5000–10,000. Typically areas of 100 μm × 100 μm were probed. Both positively and negatively charged secondary electrons have been collected for identification.

2.4. *X-ray photoelectron spectroscopy (XPS) analysis*

The samples were prepared in the glove box and transferred to the pre-vacuum chamber of the XPS instrument ($<10^{-4}$ Torr), minimizing the air exposure to about 1 min. XPS imaging has been done with an Escalab 220i instrument from Thermo VG Scientific (UK). The images have been acquired in the CRR mode, using non-monochromatic Al Kα irradiation. For each element a peak and a background image was created by selection of appropriate energy intervals in the XPS spectrum. Final images were constructed by subtracting the background image from the peak image.

2.5. *Scanning transmission electron microscopy–energy dispersive X-ray (SEM-EDX) analysis*

The samples were evacuated for at least 2 h at 150 °C, and vacuum impregnated with the standard mixture Ultra Low Viscosity Kit, hard version (Polaron Instruments Inc.). The mixture was transferred into a polyethylene capsule (BEEM), mixed with fresh embedding medium, and hardened at 60 °C under nitrogen at 0.2 MPa for several days. A cross section of an individual embedded extrudate is made using a diamond knife. The cross section is mounted on a stub with conductive carbon cement (Leit C). A conductive carbon coating was deposited by a Balzers MED10 apparatus to avoid charging in the SEM. Most micrographs have been made by the Tescan analytical SEM and some micrographs are from the LEO 1550 high resolution SEM. EDX spectra have been obtained with the Oxford INCA system.

2.6. *X-ray diffraction (XRD) analysis*

The samples were powdered and measured using a Bruker AXS D5000 reflection-diffractometer with monochromated Cu Kα radiation at 40 kV and 35 mA. A silicon single crystal was used as sample holder. Samples were rotated during the measurements. The XRD patterns were recorded using a step size of 0.02°. Phase identification was checked using the Powder Diffraction File from the International Centre for Diffraction Data (ICDD).

3. Catalyst life cycle

The life cycle of a hydroprocessing catalyst starts with the initial production of fresh oxidic catalyst (Fig. 1) [1–3], which is presulfided prior to being used in the refinery process. During its use, the catalyst deactivates and, as soon as the catalyst does not meet the performance targets within the limits of the reactor operating conditions, the reactor is shut down. Depending on the degree and nature of catalyst contamination, the catalyst can be either directly regenerated, undergo an additional reactivation/rejuvenation treatment or has to be recycled/disposed of. The regenerated catalyst, once again in its oxidic form, is again presulfided prior to further use in the refinery. The reclaimed metals for any catalyst disposed of are reused for further catalyst preparation.

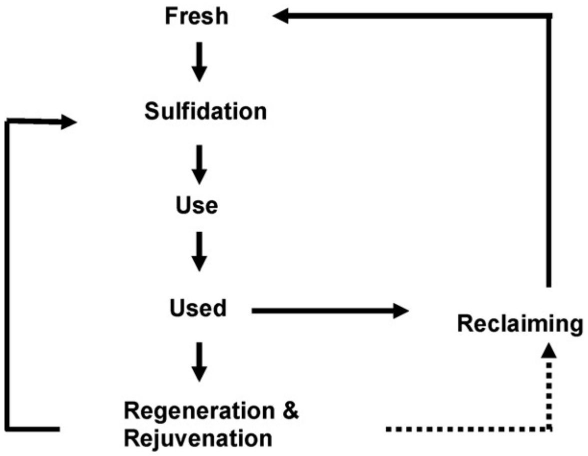

Fig. 1. Schematic representation of catalyst life cycle.

3.1. Processes and catalyst states involved in the life cycle

3.1.1. Oxidic catalyst

The manufacture of a hydroprocessing catalyst requires the preparation of the compacted (alumina) support material as well as the introduction of the active components into the support. Fresh oxidic catalyst typically contains 3–6 wt.% NiO or CoO, in combination with 15–27 wt.% MoO_3 or WO_3, supported on γ-alumina and, optionally, also components such as B_2O_3, SiO_2, or P_2O_5 [4–15]. The active metal components are present as oxides and are finely dispersed through the γ-alumina support. The compacted particles are in the form of cylindrical or shaped extrudates, pellets or beads, which are 1–5 mm in diameter. To be able to survive multiple life cycles the catalysts must be active, have stable performance, be regenerable and have excellent mechanical properties.

3.1.2. Presulfiding

Hydroprocessing catalysts are used at high temperature and pressure in the presence of H_2 and H_2S and organo-sulfur compounds [16]. Under these conditions, the finely dispersed metal oxides are transformed into sulfides [1–3], which leads to a complete rearrangement of the catalyst surface. The sulfided catalyst consists of well-dispersed MoS_2/WS_2 slabs and stacks, with edges decorated with sulfidic NiS_x/CoS_x. To get the catalyst in equilibrium with its reaction environment as soon as possible, and to ensure stable reactor performance right away from the start of a run, the oxidic catalysts are usually presulfided. The sulfidation procedure can be carried out prior

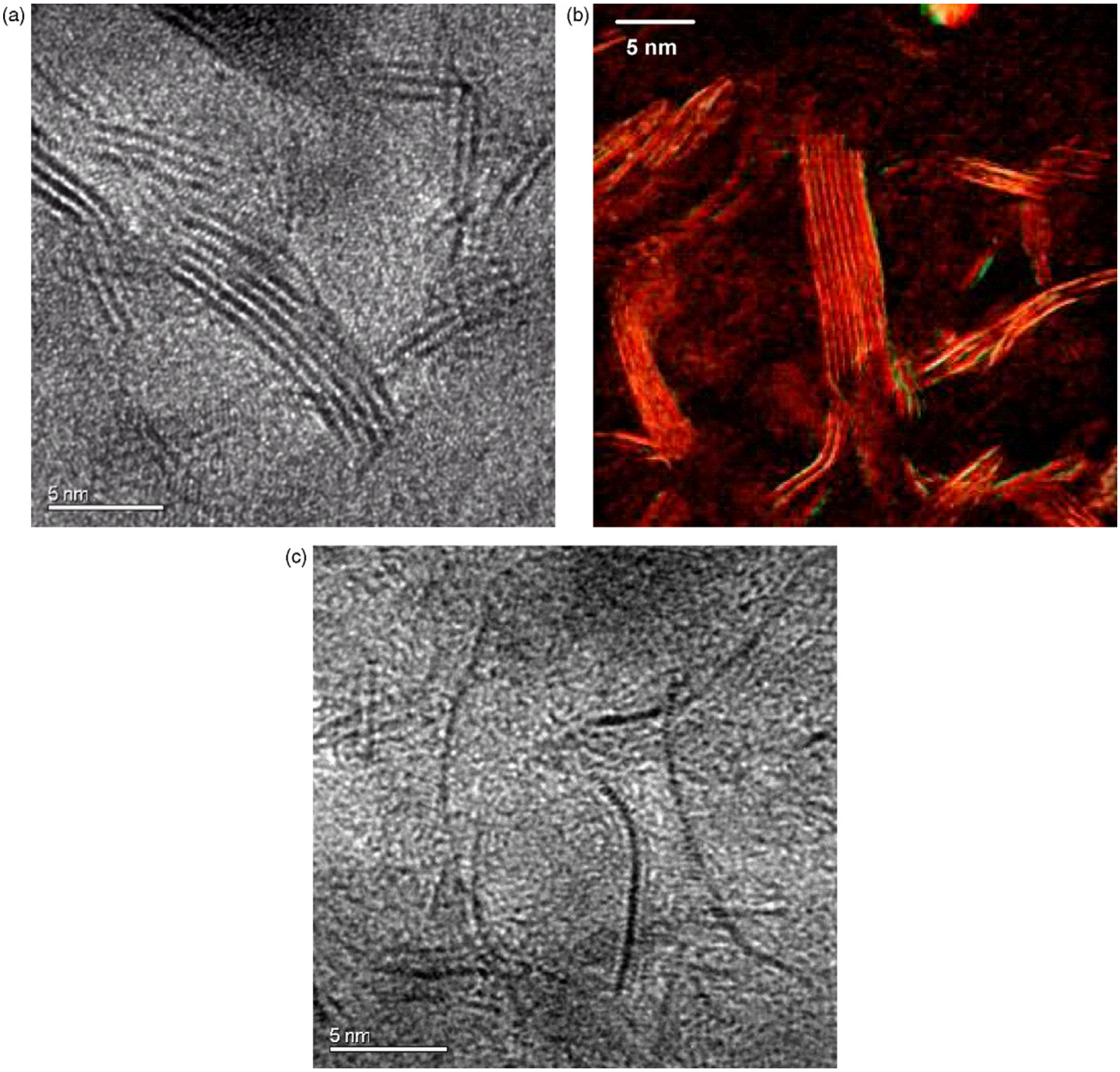

Fig. 2. Transmission electron microscopy (TEM) analysis of a freshly sulfided Ni-Mo hydroprocessing catalyst: (a) high resolution TEM micrograph showing that relatively large MoS_2 stacks are present after gas-phase sulfidation; (b) 3-D TEM image reconstruction of such large MoS_2 stacks visualized without alumina support by volume rendering (reprinted with permission from de Jong et al. [29]); (c) high resolution TEM micrograph showing curved MoS_2 single layers obtained after liquid phase sulfidation.

to (i.e. ex situ = off-site) or during the reactor start-up (i.e. in situ = on-site), by contacting the catalyst with H_2 and H_2S [17–23] or some other sulfur compound [e.g. CS_2, dimethyl (di)sulfide, organic or inorganic polysulfides, elemental sulfur] [18–20,24–26]. An important feature in sulfiding is whether either ''gas'' or ''liquid'' phase based method is used to activate the catalyst [21,23,26,27]. As illustrated in Fig. 2, catalyst sulfidation in the gas phase often leads to an increased stacking of MoS_2 slabs while catalysts after liquid phase sulfidation typically contain MoS_2 single layers [28,29]. An intermediate option is to prewet the catalyst with hydrocarbon prior to gas-phase sulfidation. The dispersion and homogeneity of the hydrocarbon prewetted and subsequently gas-phase sulfided catalyst approaches the properties of the liquid phase sulfided catalyst [30].

Ex situ presulfiding is often carried out in two steps. First, the oxidic catalyst is impregnated with a sulfur containing compound such as molten elemental sulfur [31–32] or an organic sulfur compound [33–37] dissolved in an organic solvent and dried in inert atmosphere. Under these conditions, sulfur reacts with metal oxides incompletely. The catalyst is then loaded in the reactor, to be contacted with a hydrocarbon feed and H_2 at high pressure and temperature. As the catalyst already contains sulfur, the feeds' sulfur content does not have to be increased so that the potentially difficult handling of toxic and malodorous sulfur compounds in the refinery is avoided. As illustrated in Figs. 3 and 4, the impregnation of catalyst particles with sulfur containing compounds can in some cases lead to an inhomogeneous distribution of sulfur, with the outside of the particles being sulfided while the inside is still oxidic. Another option is the complete off-site sulfidation of the catalyst [23,38–40]. This means that not only the introduction of sulfur but also the catalyst activation with H_2 is being carried out ex situ. This can be done by either impregnating the sulfur component followed by H_2 activation, or by H_2S/H_2 sulfidation. The advantage of the complete off-site sulfidation is that commercial reactor start-up is much faster since the sulfur has already completely reacted with the metals. Then it is just necessary to bring the reactor to its operating conditions without any extra time involved for presulfiding.

In situ presulfiding is carried out in the process unit's reactor [17,25,26] by contacting the oxidic catalyst at high pressure and temperature with H_2 and feed, having high sulfur content [41]. The sulfur content of the feed is often increased by ''spiking'', i.e. adding an easy to decompose sulfur compound such as dimethyl disulfide. In cases where a liquid phase sulfidation is not possible, a sulfur component such as dimethyl disulfide is injected into the H_2 stream and the catalyst is then sulfided in the gas phase. Clearly, the in situ sulfidation requires extra time during the reactor start-up. Moreover, while ex situ sulfidation processes ensure that all catalyst particles contain sulfur, in situ sulfidation may sometimes be inhomogeneous in its sulfur distribution in the catalyst bed, due to maldistribution and channeling effects occurring in large process reactors.

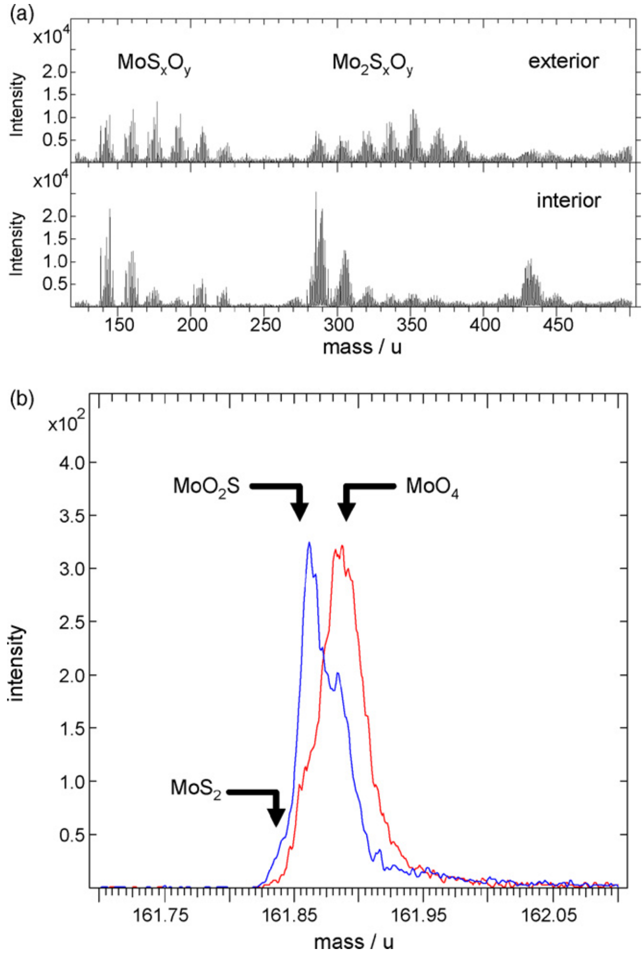

Fig. 3. Time of flight secondary ion mass spectroscopy (ToF-SIMS) results of an ex situ sulfided Ni-Mo hydroprocessing catalyst: (a) overview spectra and (b) detail analysis (red line = interior, blue line = exterior). Due to its high resolution, TOF-SIMS can differentiate between the different MoS_xO_y species present on the exterior (MoS_2 and MoO_2S) and on the interior (MoO_4) of the extrudates (negative polarity).

3.1.3. Hydroprocessing and catalyst deactivation

Crude oils are complex mixtures of saturated, unsaturated and aromatic hydrocarbons, which also contain oxygen, sulfur, and nitrogen heterocyclic compounds, as well as Ni and V metalloporphyrins [42]. During hydroprocessing, the oil is contacted with a catalyst at high temperature in the presence of hydrogen [16], where the reaction conditions used depend on process unit design as well as the oil fraction treated. Reaction temperatures ranging from 200 to 450 °C and pressures between 5 and 300 bar can be applied. Numerous reactions take place simultaneously, namely,

- hydrogenation of unsaturated hydrocarbons (HDOlef and HDA),
- (Mild) hydrocracking of large molecules (MHC),
- hydrodeoxygenation of oxygen containing molecules (HDO),
- hydrodesulfurization of sulfur containing molecules (HDS),
- hydrodenitrogenation of nitrogen containing molecules (HDN)
- hydrodemetallation of Ni and V porphyrins (HDMe).

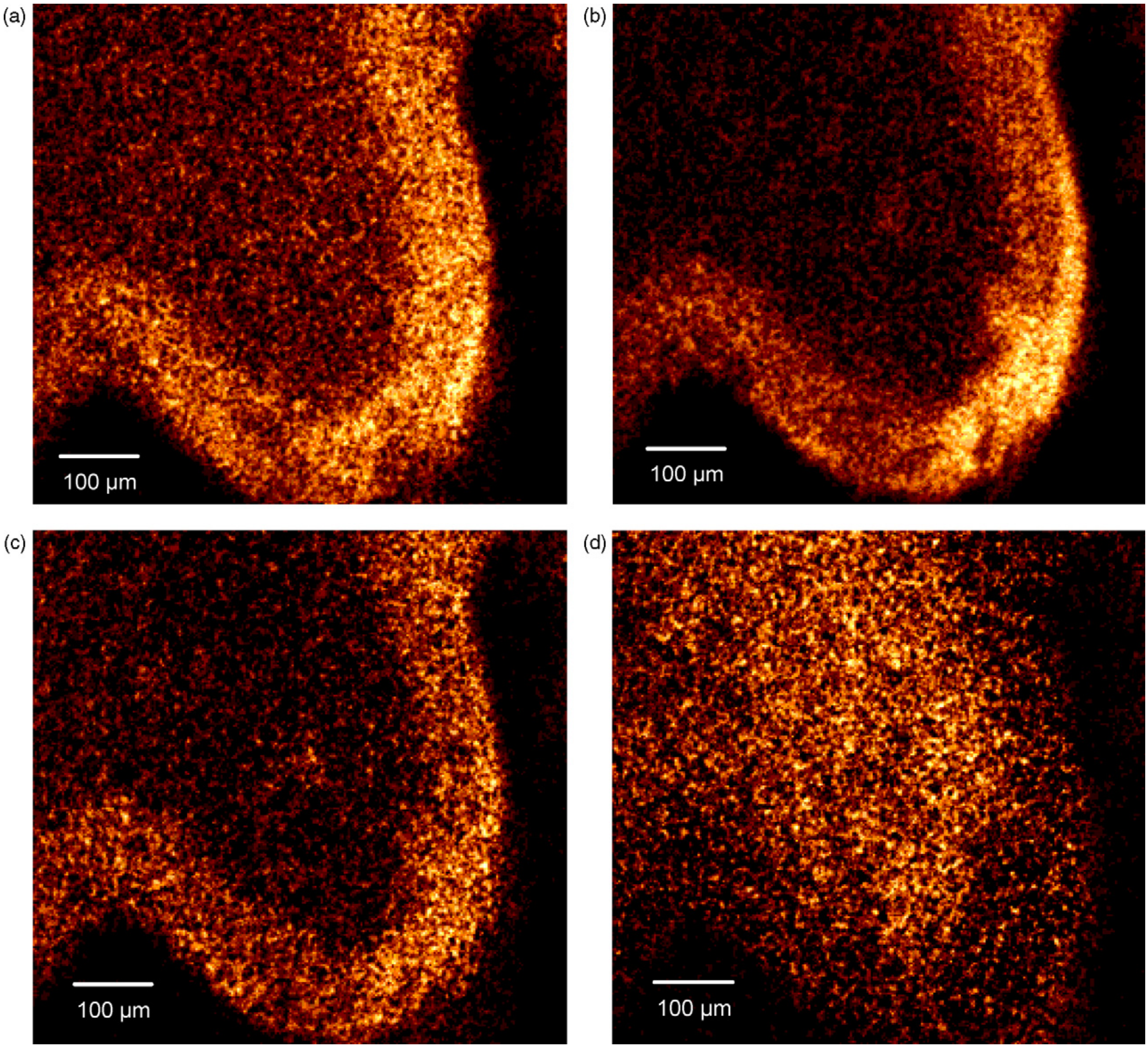

Fig. 4. X-ray photoelectron spectroscopy (XPS) element mapping of an ex situ presulfided Ni-Mo hydroprocessing catalyst: (a) C-C (1s); (b) S (2p); (c) Mo^{4+} (3p); (d) Mo^{6+} (3p). Different Mo species are present on the outside (Mo^{4+}) and on the inside (Mo^{6+}) of the extrudates. The C-C and S remnants of the organic S-compound are found predominantly on the outside of the extrudate.

HDOlef and HDA reactions reduce the portion of olefins and aromatic hydrocarbons, respectively, in the oil, while the hydrocracking reactions decrease the molecular weight. During HDO, HDS and HDN, the heteroatoms are eliminated from the molecules as H_2O, H_2S and NH_3, respectively, which can then be relatively easily removed from the reactor off-gas. Ni and V from metalloporphyrins present in the feed, become deposited on the catalyst surface.

Hydroprocessing catalysts deactivate via various mechanisms during their use, depending on the exact application and reaction conditions [1–3,43–61]. A commercial catalyst cycle length can be as long as 3–5, or even 10 years for naphtha hydrotreating units, operating on light, metal-free feeds under very mild conditions. The cycle length is typically 1–2 years for diesel, gasoline and VGO hydrotreating units. For residue hydrotreating units, operating with heavy feeds containing Ni and V metalloporphyrins under very severe conditions, the cycle length can be as short as 0.5–1 year. The most important deactivation mechanisms are sintering and segregation of the active phase [1–3], blocking of the catalyst pores [43–45] and of the active sites by coke and metals deposition [46–61], and poisoning of the active sites [46–48].

Under the reaction conditions, it has been found that the size of the MoS_2/WS_2 slabs and stacks increases (Fig. 5a), with the relative amount of NiS_x/CoS_x on the MoS_2/WS_2 edges getting very high. Since Ni/Co cannot be built in the MoS_2/WS_2 matrix, segregation of Ni_3S_2/Co_9S_8 then takes place (Fig. 5b) [1–3]. This directly lowers the catalyst's activity as seen during a life cycle. The MoS_2 sintering and Ni_3S_2 segregation seen can be quite extreme in units operated at high temperature or in units which have suffered a temperature runaway. This is illustrated in Fig. 6.

Ni and V based metalloporphyrins contained in heavy feeds decompose rapidly on the catalyst, and the crystals of Ni and V

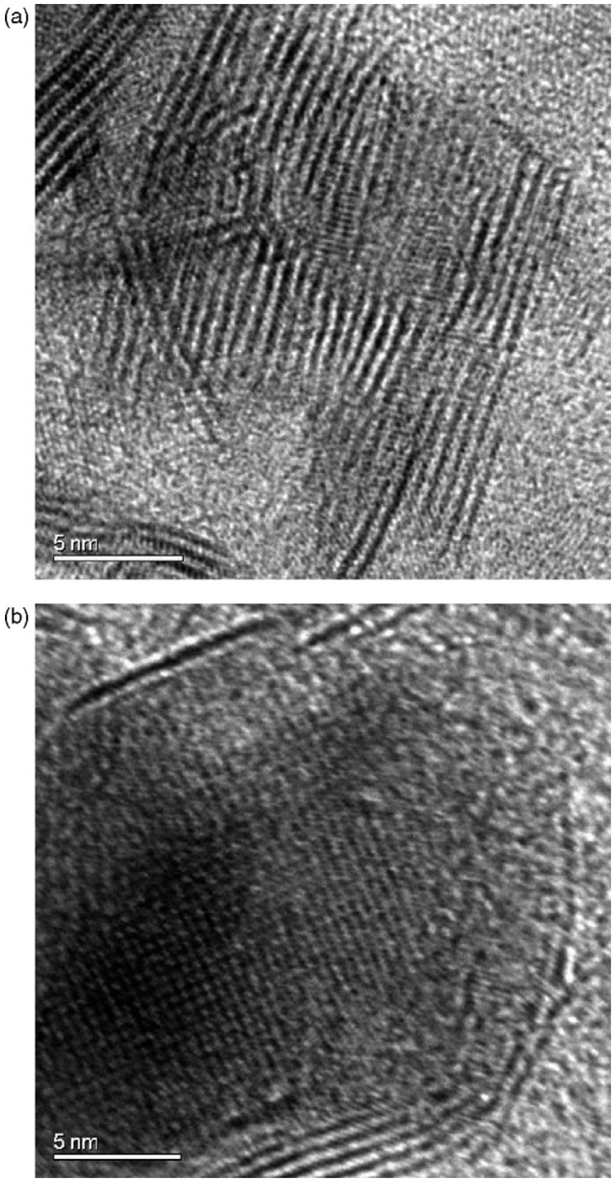

Fig. 5. High resolution TEM micrographs of a used Ni-Mo hydroprocessing catalyst. Details of: (a) MoS_2 stacks; (b) Ni_3S_2 crystal.

sulfides deposited can lead to pore blockage [49–51,54,55,62–70]. Numerous other elements, such as Pb, Si, As, Ti, Sb, Sn, Cd, Hg, Cr, Se, Ba, Ag, Cu, alkali and alkaline earth metals, may also contaminate the catalyst during the hydroprocessing catalyst's life [38,71–74]. Elements such as Pb and As specifically poison the active sites [38]. A typical catalyst contaminant is Fe originating from unit corrosion, with relatively large Fe sulfide particles being mostly found on the extrudate surface (Fig. 7).

Coke deposition [46,49,50,52–56,60,61,75–77] takes place mainly in the initial part of the run [58,59,77]. While the coke concentration remains more or less constant during the catalyst use, its composition changes. A relatively hydrogen rich, "soft" coke (i.e. cycloparafins, naphthenes and some aromatics) present at the start of run changes into hydrogen deficient, "hard" coke (i.e. dehydrogenated polyaromatics) during the further catalyst use. The coke content of used hydroprocessing catalysts is usually between 5 and 30 wt.% [78–80].

When a catalyst has deactivated beyond the acceptable level, the reactor is shut down. The catalyst's regenerability then depends on the extent of the active phase sintering and on the amount of contaminants present in the catalyst [79,81]. Typically, the used catalyst must contain less than 3–4 wt.% deposited Ni and V, with only negligible amounts of other contaminants, to be suitable for regeneration. The regenerated catalysts have to reach sufficient activity level [79–84]. Their physical (surface area, pore size distribution) and mechanical (crush strength, particle length distribution) properties must be on target as well [38,46,74,79,81]. Depending on the cause and extent of deactivation, the catalyst is either oxidatively regenerated and optionally reactivated (coke and sintering), oxidatively regenerated and leached/rejuvenated (metals deposition), or disposed of (sintering and metals deposition beyond "reparable" level). Non-residue catalysts are typically regenerated once or twice. Catalysts that are severely contaminated by metal deposits from residue and heavy vacuum gas oil applications are usually not regenerated at all and have to be disposed of/recycled [38].

3.1.4. Regeneration and reactivation

Nowadays, the oxidative regeneration is only rarely performed in situ [38,81,83] since the procedure often leads to hot spots and temperature runaways. Another problem is that the catalyst "fines" stay in the catalyst bed. Consequently, there is a danger of reactor plugging and maldistribution after the reactor restart. In most cases, the used catalyst is unloaded and oxidatively regenerated ex situ by a specialized company [38]. Good temperature control during regeneration is essential [57,85–87], being achieved through de-oiling/stripping of the catalyst [38,88], followed by air oxidation in several stages in a moving bed [80,89,90]. The catalyst is then screened to remove fines. The refinery reactor has to be re-loaded but the chance for reactor plugging/maldistribution is much smaller. Optionally, the regenerated catalyst can be sulfided ex situ prior to re-loading.

The oxidative regeneration procedure removes the coke, whilst the sulfides of Mo/W and Ni/Co are transformed back into oxides [1–3]. Stable/inactive compounds such as Ni/$CoAl_2O_4$, Ni/$CoSO_4$ or $Al_2(MoO_4/WO_4)_3$ may be formed if too high regeneration temperature is applied. Mo dispersion is restored to some extent through solid–solid wetting of MoO_3 on Al_2O_3. The regeneration can neither remove the metal deposits nor restore the sintering and segregation of Ni/Co and W components of the active phase [1–3]. After sulfidation, the regenerated catalyst once again contains MoS_2/WS_2 slabs/stacks decorated with NiS_x/CoS_x. Remainders of crystalline compounds (MoS_2, Ni_3S_2, Co_9S_8 or metal deposits) observed in the used catalyst are still present in the regenerated catalyst (Fig. 8). The dispersion and homogeneity of the regenerated catalysts are typically better than in the used catalysts, but worse relative to the fresh ones. Additional reactivation

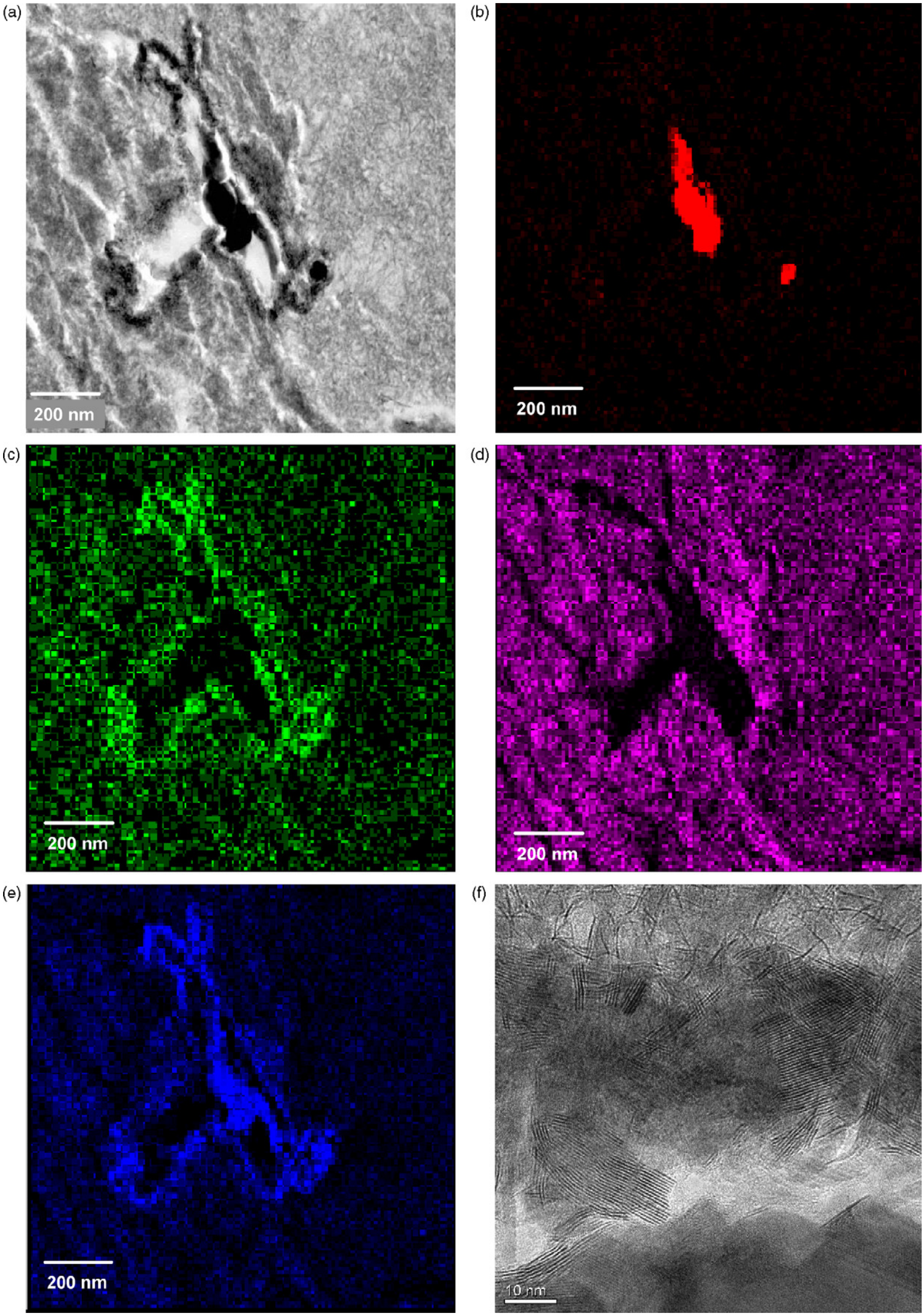

Fig. 6. Scanning transmission electron microscopy with energy dispersive X-ray (STEM-EDX) analysis of a used Ni-Mo hydroprocessing catalyst: (a) STEM image; the corresponding (b) Ni-K (red); (c) Mo-K (green); (d) Al-K (purple) and (e) S-K (blue) elemental maps showing a very large Ni_3S_2 crystal surrounded by large MoS_2 stacks; (f) TEM micrograph showing the boundary between a Ni_3S_2 crystal and the surrounding MoS_2 phase.

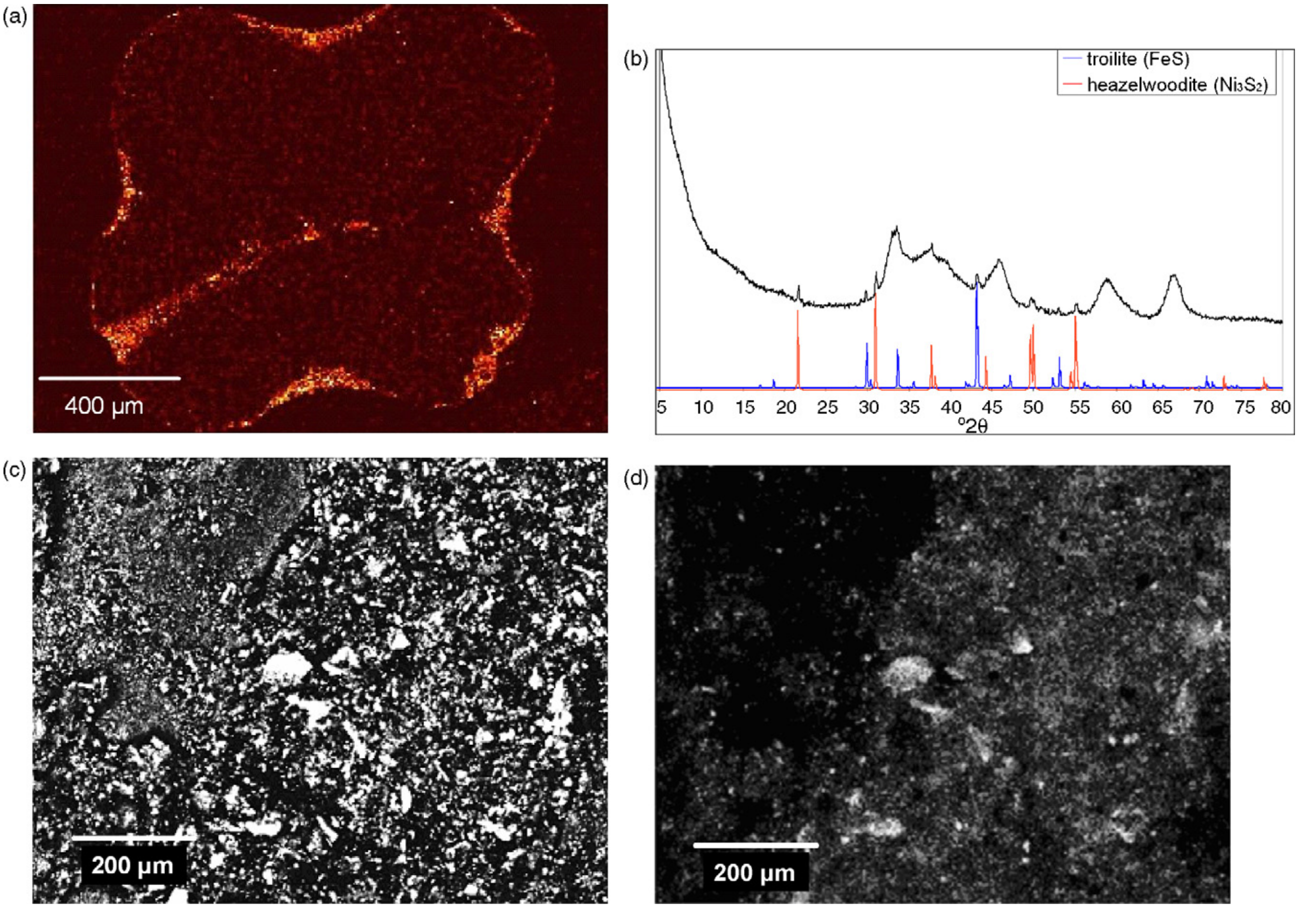

Fig. 7. Scanning electron microscopy energy dispersive X-ray analysis (SEM-EDX) and X-ray diffraction (XRD) analysis results of a used Fe-contaminated Ni-Mo hydroprocessing catalyst: (a) Fe-K map of an extrudate cross-section; (b) XRD spectrum; (c) SEM back-scatter image of the extrudate surface; (d) the corresponding Fe-K map. The images and SEM-EDX maps show that Fe sulfide deposits are concentrated on the surface of the catalyst extrudates. The presence of FeS (troilite) is confirmed by XRD.

treatments are available to further redisperse the active phase and to remove any leftover crystalline compounds [22,87]. The dispersion and homogeneity of the reactivated and subsequently re-sulfided catalyst approaches the properties of the fresh sulfided catalyst (Fig. 9).

3.1.5. Additional treatments for used residue catalysts

An additional rejuvenation treatment can be applied for regenerated catalysts mildly contaminated with Ni and V deposits [46]. One example is the selective removal of V and other mineral deposits on the exterior of the catalyst pellets by attrition [57,84], or a selective leaching of the contaminants with various solutions [57,91–96]. Another option to improve the regenerated catalyst performance is with an additional impregnation of the active components [97,98]. Catalyst particles severely contaminated with metal deposits can also be eliminated by density separation [84].

3.1.6. Catalyst disposal and recycling

The used catalyst is disposed of when the performance cannot be brought to the desired level or if the mechanical properties strongly deteriorate upon regeneration/rejuvenation [74]. Alternatives to disposal are catalyst reuse in less demanding refinery operations [99] or as a hot gas clean-up sorbent (e.g. to remove H_2S) [74,100,101]. The commodity prices of metals fluctuate strongly and the exact way of disposal depends on the economics of the moment [46,74,84]. Moreover, environmental legislations require comprehensive solutions for the disposal of spent catalysts [78,102] since today only ‘‘ultimate’’ wastes may be dumped. If the catalyst has to be disposed of as solid waste it is necessary to form an inert non-leachable solid suitable for storage [46,74]. This can be done by either encapsulation or by stabilization [103–105]. At present, relative to the early 1990s, the prices of Ni, Mo and W are at an extremely high level, while the price of Co is more or less unchanged (Fig. 10). This means that the cost price of metals used in the production of typical Co-Mo, Ni-Mo and Ni-W catalysts has increased over the past 15 years by a factor of 3.6, 6.5 and 5.1, respectively. Consequently, while in the past a fee had to be paid to the metal reclaimer or to the spent catalyst broker to dispose of the catalyst, today a spent catalyst has a market value as a ‘‘metal source’’. The high metal prices have resulted in a clear trend towards catalyst recycling, which is typically carried out by pyrometallurgical processes [46,74,78,84,95].

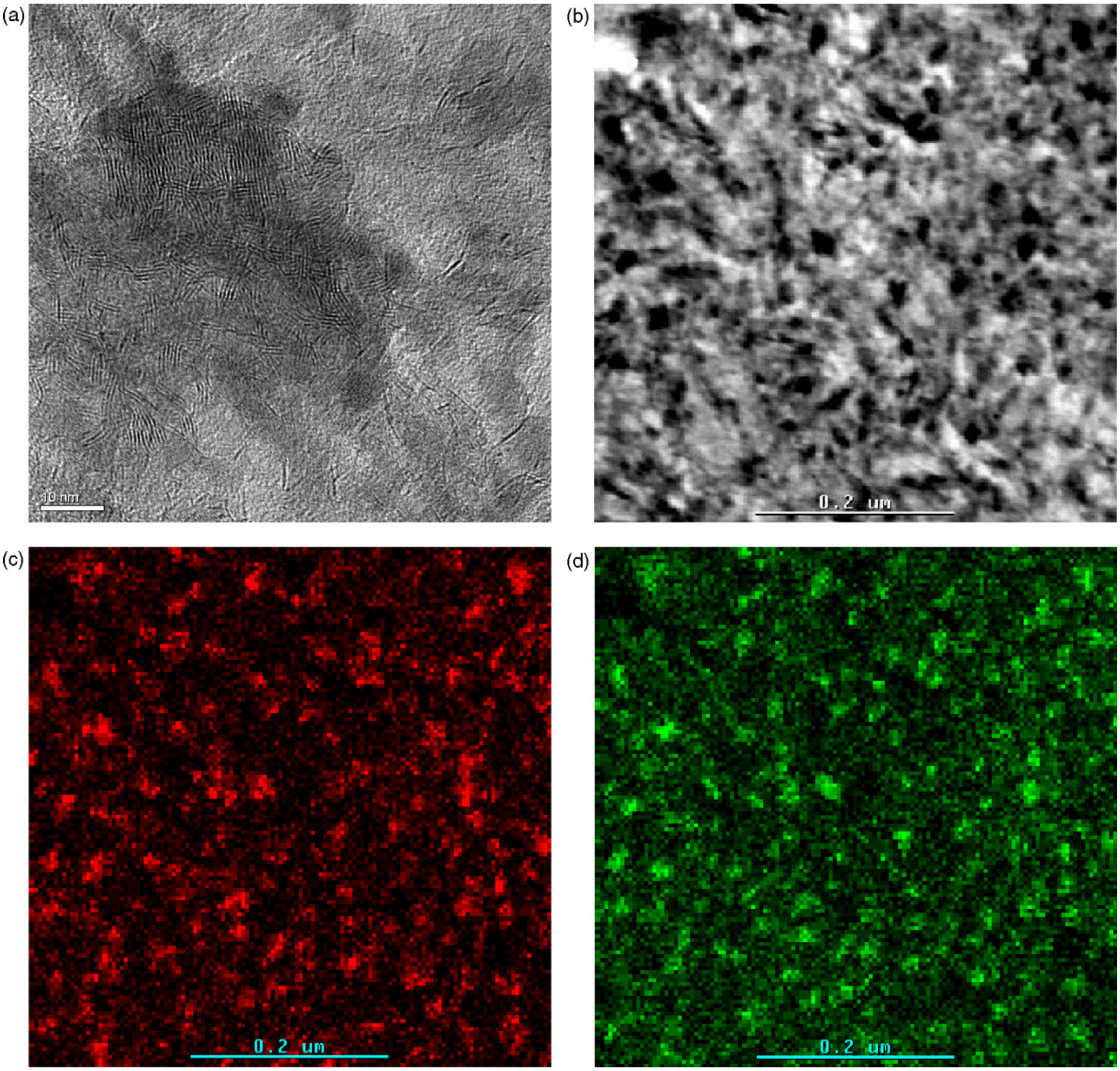

Fig. 8. STEM-EDX analysis of a regenerated Co-Mo hydrotreating catalyst: (a) TEM micrograph showing a large conglomerate of MoS_2 stacks mixed with small Co rich particles; (b) STEM image of a larger area containing such conglomerates; the corresponding (c) Co-K (red) and (d) Mo-K (green) maps.

4. Effective and responsible management of catalyst life cycle [78,102]

As discussed above, the catalyst life cycle typically involves a long chain of operations, normally performed by different specialized companies. Besides manufacturing, these operations include transportation, loading, presulfiding, turnaround optimization, change out, regeneration, used catalyst brokering, metal reclaiming, as well as supplying different chemicals and materials. The multiplicity of steps, the high number of different companies as well as technical, logistic and environmental issues involved makes it imperative to manage the catalyst life cycle in the most efficient and responsible way.

In the past, each of the consecutive steps in the catalysts' life was typically handled by a different company, under the direct coordination of the refinery. Such an approach suffers from a main disadvantage, *i.e.*, these operations fall outside the refineries' core business (oil refining). In addition, as refineries are consequently increasingly cutting costs and resources, change-outs and overhauls are becoming more and more challenging. Since the intervals between turnarounds tend to increase, the experience required for efficient change-outs is becoming less available. The level of personnel turnover and job market fluidity exacerbates this issue.

To address the above logistic and technical pinch points leading catalyst manufacturers have started to provide "catalyst management" services to their refinery customers. The objective of these services is to support all refineries' needs associated with the use of refining catalysts. The main advantage of this approach resides in the fact that these specialized services are strictly linked with the core activities of catalysts manufacturers. Catalyst management services are

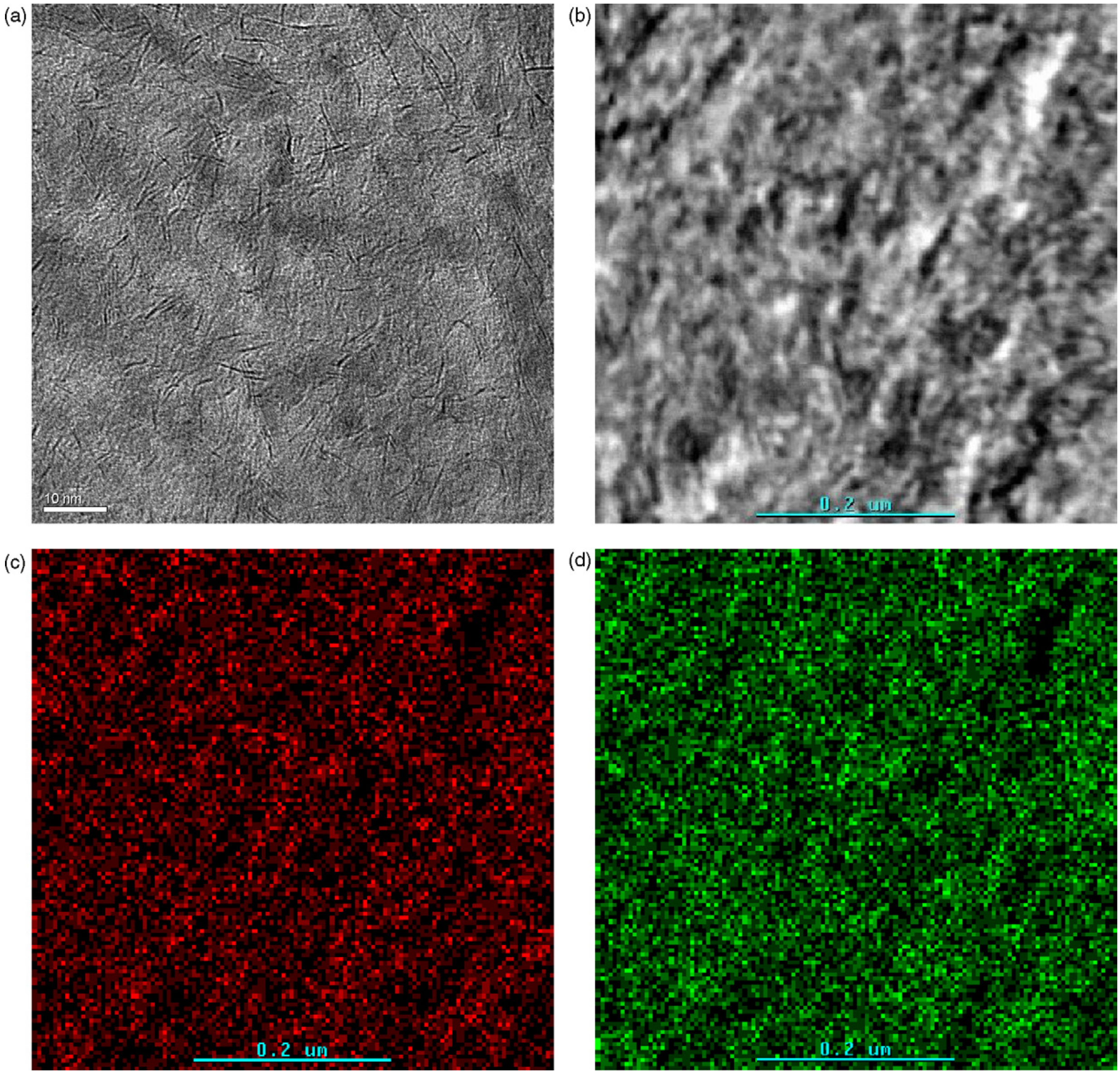

Fig. 9. STEM-EDX analysis of a reactivated Co-Mo hydrotreating catalyst: (a) TEM micrograph; (b) STEM image; the corresponding (c) Co-K (red) and (d) Mo-K (green) maps. High MoS_2 dispersion and no Co rich particles are observed in the reactivated catalyst.

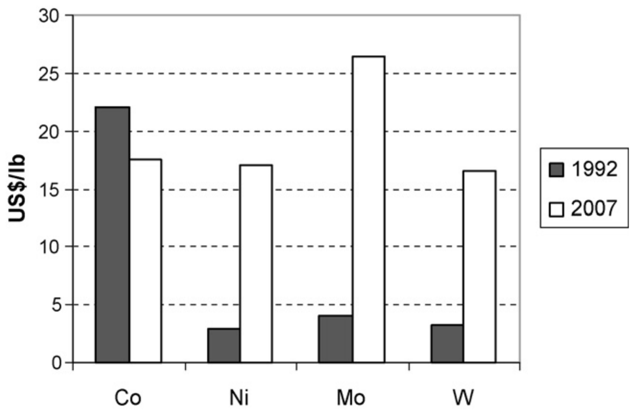

Fig. 10. Changes of base metal prices over the past 15 years.

gaining in popularity and the market is increasing steadily over the last 10 years. An example of such services is the ‘‘Total Catalyst Management’’ (TCM), offered by Albemarle Catalysts (catalyst manufacturer) [102,106].

4.1. *Total Catalyst Management (TCM) provided by Albemarle Catalysts [102,106]*

Professional catalyst life cycle management like TCM accompanies the catalyst through its whole life, from procurement to final recycling. TCM, in particular, is a flexible package of products and services, which are selected in close co-operation with the refinery. In this program, Albemarle co-operates with UOP (recent alliance in Hydroprocessing), Eurecat (presulfiding and regeneration), and Petroval [(un)loading] as strategic

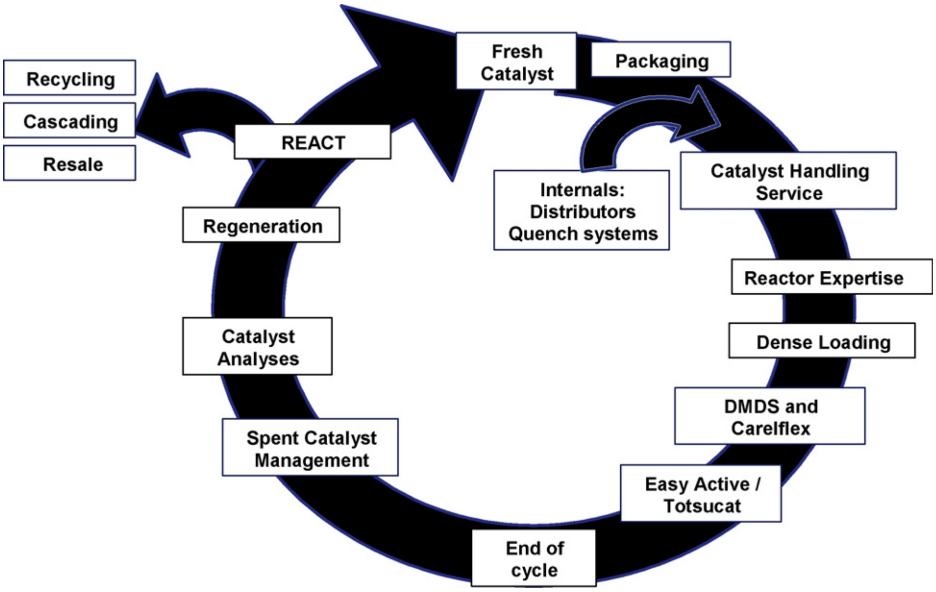

Fig. 11. Total catalyst management (TCM) full service cycle (typical services offered).

partners. Additional (qualified and experienced) service providers are selected based on customer requirements, economic and geographical grounds.

The whole range of services included in the management package is shown in Fig. 11. These include:

1. fresh catalyst delivery and classical technical service,
2. catalyst handling service, including (un)loading and change-out planning and co-ordination
3. selection/offering of optimal reactor internals,
4. ex situ or in situ presulfiding,
5. catalyst quality evaluation,
6. regeneration and reactivation,
7. recycle co-ordination,
8. catalyst performance prediction and extended technical services,
9. catalyst pooling, storage, resale and emergency insurance
10. technology, optimization and training,
11. radioactive tracer-scanning services to troubleshoot liquid flow in fixed bed reactors.

One of the new services offered as a part of the TCM is the PROTECT^{TM} treatment for STARS catalysts. The superior performance of STARS^{TM} catalysts is possible because of the highly active Type II sites. The full benefit of STARS^{TM} catalysts is realized by utilizing liquid feedstock during the activation procedure. The liquid feedstock helps to maintain the active sites in a Type II configuration. However, some units have reactor pressurization limitations that prevent them from adding liquid to the unit during catalyst activation. PROTECT^{TM} treatment is specifically developed to enable gas-phase sulfiding of STARS^{TM} catalysts. PROTECT^{TM} treatment coats the STARS^{TM} catalyst with a waxy hydrocarbon and thereby keeps the active sites in their Type II configuration during the gas-phase activation. The waxy hydrocarbon will be removed from the catalyst at temperatures above 480 °F (250 °C) during the in situ presulfiding.

Reactivation is, in particular, an emerging service offered within TCM. A special reactivation technology (REACT^{TM}) has been developed by Albemarle and Nippon Ketjen, aimed at restoring the original activity of the Type II active sites for the STARS^{TM} catalysts. REACT^{TM} technology is a catalyst rejuvenation treatment that enables the activity of regenerated STARS^{TM} catalyst to be recovered to over 90% when compared with fresh catalyst. REACT^{TM} technology redistributes the metals and reconfigures the active sites to the Type II formation of the original STARS^{TM} catalyst.

In the past years, the "catalyst management" approach has been very successful in a number of countries and for different companies. The number of recent TCM deals increased from 11 in 1999 to nearly 30 in 2006. In all cases the quality expectations have been exceeded and stringent time schedules have been met.

5. Conclusions

The commercial life cycle of hydroprocessing catalysts involves numerous technical, logistic and environmental issues in each of its stages. While in the past this complex process was mostly handled by a long chain of different consecutive users and service providers, there is a clear trend towards the management by a single co-ordinator. The catalyst manufacturer, who (as a chemical company) has an extensive knowledge of environmental legislation and regulations related to catalyst handling, provides the most logical choice as the catalyst life cycle co-ordinator.

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