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Sustainable Management of Spent Hydroprocessing Catalyst

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Increasing demand for high-quality transportation fuels and stringent environmental standards have resulted in the significantly increased quantity of spent hydroprocessing catalysts, which require the sustainable management. To minimize the generation of hazardous wastes, the spent hydroprocessing catalysts can be regenerated via oxidative regeneration or reactivated via the rejuvenation process. If the catalytic activity cannot be restored, it can be utilized as a source of other useful materials, and/or metals in the spent catalyst are recovered. Finally, the stabilized residues shall be disposed by using an environmentally sound method.

Keywords: Sustainable Management; Spent Hydroprocessing Catalyst; Oxidative Regeneration; Rejuvenation; Metals Reclamation

Introduction

Increasing demand for high-quality transportation fuels and stringent environmental standards have resulted in the significant growth of the use of hydroprocessing catalysts globally. It is expected that the amount of spent hydroprocessing catalysts produced will be 200,000 tons annually with an anticipated 5% annual increase [1]. Therefore, the sustainable management of these spent catalyst wastes will reduce the pollution to the environment and increase the economic efficiency of the hydrogenation process.

Hydroprocessing catalysts generally include hydrotreating and hydrocracking catalysts. The most used hydrotreating catalysts are molybdate (Mo) supported on alumina (Al_2O_3) and promoted by cobalt (Co), nickel (Ni) or tungsten (W), while hydrocracking catalysts are bifunctional, and consisting of active metals (like Mo, Pt, and Ru) supported on a zeolite (*e.g.*, ZSM-5). The catalyst life varies for different applications: 1-2 years for hydroprocessing of atmospheric gas oils or vacuum gas oils, 0.5-1 year for hydrotreating resid, 5-10 years for a naphtha hydrotreater using straight run feed [2], and ~2 years for hydrotreating bio-feedstock [3, 4].

When the performance of the catalysts cannot meet the desired level, they will be unloaded and examined for its regenerateness. After regeneration, the regenerated spent hydroprocessing catalysts will be re-evaluated. Catalysts of a good quality are pooled and re-sulfided for reusing, while catalysts with a lower quality could be reused in less critical

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applications. For the spent catalyst has lost its regenerateness, the metal in the spent catalyst will be recycled to the maximum extent. The residues are disposed by using an environmentally sound method.

Oxidative Regeneration

Oxidative regeneration is mainly used to burn off the coke deposited on the spent hydrotreating catalysts and transform metal sulfides back into their oxides. But it could not recover the structural properties to the same level as the fresh catalysts. Typically, the spent catalyst should not contain more than 2-3 wt% of metal contaminants (mostly Ni and V) to be suitable for oxidative regeneration [5].

This regeneration process is affected by multiple factors including O_2 supply, the composition of the coke, and mass transfer. Air generally provides a good O_2 source. However, the uncontrolled temperature increase may lead to sintering of the catalyst. Under certain circumstances, diluted air may be more suitable.

The temperature is the most critical factor. It is found that a complete removal requires burning at the high temperature of ~450°C, if burning the sulfided spent CoMo catalysts [6]. Oxidation of sulfidic sulfur and organic sulfur resulted in the release of SO_2 at 250°C and 450°C, respectively. Oxidation of carbon also happens at ~450°C [7]. More severe oxidation conditions are needed for the NiW catalyst, because of the lower oxidation activity of NiO and WO_3 compared to Co_3O_4 and MoO_3 [8]. The removal of sulfidic sulfur from the spent NiW catalysts as SO_2 happened at 227-327°C and the removal of carbon as CO_2 or CO occurred at 377-577°C.

The shapes of the catalysts establish the mass transfer limitations, which may be minimized by grinding the deactivated catalyst to a fine particle size [9, 10].

The oxidative regeneration can be carried out in situ or ex situ. The conventional in-situ technique burns off the coke and re-sulfides the catalyst in the hydrotreating reactors. Regeneration is performed by injecting a stream of diluted air with nitrogen or steam to remove coke and reversible poisons like sulfur and nitrogen by oxidizing them at temperatures between 450-550°C into gaseous CO, CO_2, SO_x, and NO_x. The process parameters such as air concentration and temperature are carefully controlled to prevent runaway combustion [11]. Following regeneration, sulfiding converts the metal oxides impregnated onto the catalyst support into the corresponding metal sulfides, and forms H_2S that can enter the process water to be removed. According to environmental regulations, acidic gases must be neutralized, and the neutralization process is time-consuming and requires injection systems, trained operators, and time. Forth more, in-situ regeneration requires long unit downtime and gives poor activity recovery due to uneven gas flow [12].

The ex situ (also called off-site) oxidative regeneration has been widely accepted by the petroleum refining industry in the 1990s, because it provides benefits on safety, time savings, and less environmental problems caused by generating SO_x and CO_x. Better activity recovery can be achieved by the ex situ regeneration, because it allows performing more than one cycle with the same catalyst batch [13]. The reactor corrosion due to the formation of acidic gases is eliminated. The chance for accidents, hot spots, and reactor malfunction is lower. Dedicated catalyst specific regeneration procedures can be applied, and the fines can be removed by screening. The costs of the oxidative ex situ regeneration are around 20% of the fresh catalyst price [14].

Rejuvenation

The rejuvenation of spent catalysts, also known as reactivation or reactivation, is additional processes that may be required. Oxidative regeneration is typically performed on older generation Type I catalysts, with recovered activity in the range of 70-85% of fresh activity, depending on the degree of metals contamination and surface area. For more recent generation catalysts containing the highly active Type II sites, the oxidative regeneration of Type II catalysts only results in a mediocre activity recovery. One possible reason for this low-activity recovery is that these catalysts have not been exposed to the temperatures that are required to restore their activities. The rejuvenation process developed by Porocel [15] consists of two steps: an initial thermal regeneration to remove the carbon and sulfur, followed by a proprietary chemical treatment to remove the inactive crystalline compound such as β-$CoMoO_4$ or $NiMoO_4$, re-disperse the metals, and restore the Type II active sites for maximum activity recovery. These treatments typically use some oxygen containing compounds that play the role of chelating agents and thus may help re-disperse the metals [16]. Rejuvenation of the spent catalyst may restore greater than 90% of fresh catalyst activity and provide the spent catalysts that meet certain physical and chemical criteria.

Reuse of the Spent Catalysts

Reuse of a regenerated spent catalyst to maximize the catalyst life is the key to the sustainable management. The regenerated catalysts may be suitable for less demanding refinery operations. Typically, the regenerated gas oil hydrotreating catalyst might be used for hydrotreating of kerosene, and the regenerated Kerosene hydrotreating catalyst can be applied for naphtha hydrotreating [17].

It’s also possible to use at least a small portion of spent catalysts for the preparation of useful materials like fused alumina, Anorthite glass-ceramics, and abrasive material [18]. Depending on the remaining porosity and surface area, spent catalysts may still have potential especially, in some gas-solid applications, *e.g.*, used as a H_2S clean-up sorbent [19].

This kind of catalyst management services could provide sustainability to the global catalyst inventory through a pool where each site or unit will take the required catalyst quantity corresponding to their need.

Metals Reclamation

When the spent catalyst reaches the end-of-cycle, *i.e.*, the desired level of activity could not be restored, or the mechanical properties would strongly deteriorate during regeneration. Metals reclamation could remove toxic components and make further dispose of residues possible [20].

There are two types of reclamation processes: hydrometallurgy and pyrometallurgy. The hydrometallurgical reclamation involves the solubilization of metals via roasting, followed by a selective leaching of metals of interest [21]. Literature regarding the hydrometallurgical reclamation of metals is extensive, and has been reviewed by Furimsky [21] and Marafi and Stanislaus [18, 22].

The pyrometallurgical process starts with melting dry catalysts in a furnace at temperatures around 1200-1500°C [23]. Heavy metals sink to the bottom as alloys containing the alumina or silica support, which are further separated from the slag. Pyrometallurgical processes for recovering metals (like Pt and Pd) in hydrocracking catalysts involve chlorination at high temperatures (900-950°C) for recovery of platinum and other metals as volatile chlorides, which is followed by heating at high temperatures (800°C) in a gas flow containing water [24].

CONCLUSIONS

As the energy demand continues to rise and the environmental regulations are more stringent, the increasing quantity of spent hydroprocessing catalysts requires the sustainable management, which has a goal of minimizing the generation of hazardous wastes. The spent hydroprocessing catalysts can be regenerated via oxidative regeneration and re-sulfided or reactivated via the rejuvenation process, if it meets the requirements of the regenerateness. If the catalytic activity cannot be restored, it can be utilized to make other useful materials, and/or metals in the spent catalyst are recovered. Finally, the stabilized residues of spent hydroprocessing catalysts can be disposed in landfills.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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