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Minimization of Waste Spent Catalyst in Refineries

Chiranjeevi T*, Pragya R, Gupta S., Gokak DT, Bhargava S

Corporate R&D Centre, Plot No. 2A, Udyogkendra, Surajpur, Greater Noida, India

Abstract

Solid catalytic materials play major role in oil refining industry. There are various types of catalysts which are in use but the major ones are mainly hydroprocessing catalysts, Fluid catalytic cracking catalysts and reforming catalysts. During processing, catalysts gets contaminated with impurities viz coke, sulfur, vanadium and nickel in the crude oil feed and becomes deactivated over a period of time. Diesel hydrodesulfurization catalysts typically have life cycle of 3-4 years where as FCC catalysts gets lost to atmosphere on daily basis and is offloaded fortnightly / monthly based on activity. Once catalysts completes their life cycle they will be withdrawn from the process, at this stage, catalysts are considered “spent” and the heavy metals, coke, and other poisonous elements make them as hazardous waste. As per literature Dufresne estimated that the total quantity of spent hydroprocessing catalysts generated worldwide is in the range of 150,000 to 170,000 tons per year. Therefore, with anticipated 5% annual increase in catalyst consumption, the generation of spent hydroprocessing catalysts predicted to be 200,000 tons annually. The exact figures of spent FCC catalysts are not available but considering the short life span of the catalyst and 400 FCC units operating across the world volumes assumed to be very high. Significant increase of spent hydroprocessing catalysts volumes are mainly attributed to rapid growth in the distillate hydrotreating capacity to meet the increasing demand for ultra low sulfur transportation fuels, reduced cycle times due to in increased severity operations to meet stringent fuel specifications and demand of processing sour crudes based on economic criteria.

The traditional way of disposing the spent catalysts is land filling which is not environmentally friendly and occasisionally it leads to ground water contamination. Various options to reduce the generation of hazardous waste spent catalyst are using highly active catalysts, regeneration of the catalysts and reuse of the spent catalysts in other processes. The present paper will discuss about alternate ways of using spent catalyst by taking case study of hydroprocessing catalysts and thereby minimizing the waste spent catalyst in refining industry.

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Keywords: Waste minimization, Hydrotreating catalysts, Catalyst regeneration, CoMo or NiMo catalysts, Spent catalysts;

* Corresponding author.
E-mail address: chiranjeevit@bharatpetroleum.in

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1.0 Introduction

Varieties of catalysts are used in the petroleum refinery operations to improve the process efficiency. The catalysts often contain chemicals (e.g. metals, metal oxides, metal sulfides, inorganic support), which facilitate hydrocarbon transformations with high selectivity and permit the refiners to produce full range of clean transportation fuels and other chemicals with desired specifications from petroleum distillates and residues. The catalysts used in the refining processes deactivate with time due to structural changes, poisoning or deposition of extraneous materials like coke and metals. The volume of spent hydroprocessing or hydrotreating catalysts discarded as solid waste has increased significantly in recent years due to the following reasons: (i) A rapid growth in the distillates hydrotreating capacity to meet the increasing demand for ultra-low sulfur transportation fuels. (ii) Reduced cycle times due to higher severity operations in hydroprocessing units. (iii) A steady increase in the processing of heavier feed stocks. (iv) Rapid deactivation and unavailability of reactivation process for latest residue hydroprocessing catalysts [Silvy RP, 2004]. The total quantity of spent hydrotreating catalysts generated worldwide is in the range of 150,000–170,000 t/year [Dufresne,2007]. Disposal of spent catalysts requires compliance with stringent environmental regulations. Spent hydroprocessing catalysts have been classified as hazardous wastes by the environmental protection agency (EPA).

As a result of the stringent environmental regulations on spent catalyst handling and disposal, research on the development of process for regeneration and reuse of waste hydrotreating catalysts has received considerable attention. Furimsky, 1996, reviewed the environmental, disposal and utilization aspects of spent refinery catalysts and the various options suggested (a) minimizing spent catalyst waste generation (b) utilization to produce new catalysts and other useful materials, (c) recycling through recovery of metals and (d) treatment of spent catalysts for safe disposal, are available to refiners to handle the spent catalyst problem. Traditionally catalyst activity was restored and reused by in-situ regeneration. In-situ regeneration includes coke burning step and activation treatments which were performed in the user's reactor. During coke burning step other pollutants like nitrogen, sulfur (which is also part of active phase) are oxidized to CO, CO_2, SOx and NOx. Activation of catalyst is done by sulfidation of metal oxides to metal sulfides which causes excess H_2S gas handling at refinery site [Patrick, Sal Torrisi, 1999].

Current paper highlights the concept of waste minimization by regenerating and re-use of spent catalyst which is due for disposal by taking hydroteating catalyst as a case study. One commercial spent catalyst was regenerated in the lab and based on lab results, catalyst was recommended for ex-situ regeneration. Ex-situ regenerated catalyst properties were compared with lab regenerated catalyst and found that properties are having close match. The plant performance data of ex-situ generated catalyst was compared with catalyst performance before regeneration to assess the level of deactivation.

2.0 Experimental Details

2.1 Textural Properties

Surface area and pore volume of the catalyst samples were determined using nitrogen adsorption-adsorption measurement technique by Autosorb -1MP (Quanta chrome, USA) at -196^{o}C (ASTM No: 3663-99). Prior to the measurements, the sample (100 mg) was degassed at 300^{0}C for 3 hours under vacuum (10^{-3}torr). Surface area for the sample was estimated by analyzing the adsorption data in the relative pressure (P/P0) range of 0.05 to 0.3 using BET method.

2.2 Mechanical Properties

Bulk density of the sample was estimated using Duel Auto Tap density meter supplied M/s Quantachrome, USA as per ASTM D 4164. Bulk crushing strength was measured by using test unit supplied by M/s.Vinci, France as per Shell Method, SMS 1471. Particle size of spent regenerated and fresh catalyst was carried out by sieve analysis and also by using standard vernier calliper equipment.