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Utilization of Spent Catalyst (Solid Waste) from the Nitrogeneous Chemical Plant

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ABSTRACT

Nitrogeneous fertilizer industry generated so many spent catalysts during the manufacturing of fertilizer's. In production of ammonia and other products, different types of catalysts are used. After periodically use of the catalyst due to the poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst, they will become inactive. In such cases fresh catalysts have to be substituted and the spent catalyst will be discarded as waste material. Spent catalyst waste reduction at source can be achieved by using improved more active and more stable catalysts, regeneration and reuse of deactivated catalysts in many cycles, before the final disposal. The spent catalyst can be recycled by using them as raw materials for recovery of valuable metals and other products.

Key words: Spent catalysts, Disposal, Regeneration, Nitrogeneous fertilizer, Metal recovery, Roasting, Hydrometallurgy.

INTRODUCTION

More than 99% of world nitrogen fertilizer production is based on ammonia (NH_3). Ammonia is basically produced from water, air and energy. The source of energy is normally coal or hydrocarbons which are reacted with water at high temperature and electricity to drive the compressures. Naturals gas is generally the preferred hydrocarbon. Some 77% of world ammonia prodution capacity is currently based on natural gas.

Nitrogeneous fertilizers industry is one of the major industries in the India. The industry is uniformaly scattered throughout the country and is very friendly to the nation as it related to the enhanced food production needed for the growing population.

In the nitrogeneous fertilizer industry, for the production of ammonia and other products, different types of catalysts are used. These catalyts are given in table -1. All these catalysts have an active life from 5 to 7 years, on the most of which it is deactivated and must be replaced.

The amount of spent catalysts discarded as solid wastes, has increased significantly in recent year's, because of a steady increse in the processing of heavier feedstocks containing higher sulphur, nitrogen and metal contents, together with a rapid growth in the distilates and fertilizer industries. The storage, transportation, treatment and disposal of spent catalsyts require compliance with 'stringent environental regualtion because of their hazardous nature. As a result, increasing attention has been paid to minimize spent catalyst waste generation at source as well as develop safe and cost effective method for recycling and disposal.

Regeneration /reactivation and reuse

The quantity of spent catalyst discarded as solid wate can be reduced, if the useful life of the catalyst before disposal could be extended for a longer period. This can be done in three steps (1) Regeneration, and reuse (2) usage in less demanding proceses (3) reduce catalysts consumption by using improved catalysts with longer, life.

Spent catalysts of fertilizer plant consists of oxide of Zn, Co, Mo, Ni, Fe, Cu, Cr on Al_2O_3 support. During use in a production of ammonia, the catalysts deactivate mainly by the deposition of oil, coke and foreign material, which cover's the active sites. Catalysts deactivated by simple coke and deposition can be reused after regenerating the catalysts by removing the deposit coke by combution. This can be repeated a few times until the catalyts activity recovery is reduced below acceptable level because of loss of surface area caused by sintering during regeneration. Careful control of temperature and oxygen concentration during coke burning is critical to suppress the sintering of the active phase and support (furismsky and massoth 1993). Total removal of poisons is often difficult, and even residual traces may decrease activity as the catalyst is brought back on line. However, if some deactivation is acceptable, regeneration is preferred. Removal may invovle only increasing temperature or may involve treatment with a chemical that reacts with the poison or competes with the poison for active sites. Catalyst deactivation is seen to result from fouling, thermal reorganization or poisoning. Overall, catalyst regeneration is always preferred even if the catalyst is some what less active. Poisoning can often be reversed where as thermal reorganization is usually irreversible.

Table 1: Catalysts used in Nitrogenous fertilizers plant for production of ammonia

S. No.	Process	Catalysts	Nature of spent catalyst
1.	Hydrosulfurization	$CoO-MoO-Al_2O_3$	Pyrophoric
2	Desulfurization	ZnO	Non pyrophoric
3	Primary reforming	$NiO-Al_2O_3$	Pyrophoric
4.	Secondary reforming	$NiO-Al_2O_3$	Pyrophoric
5.	High temperatre shift	$Fe_2O_3-Cr_2O_3$	Pyrophoric
6.	Medium temperature shift	$CuO-ZnO -Cr_2O_3$	Pyrophoric
7.	Low temperature shift	$CuO-ZnO-Al_2O_3$	Pyrophoric
8.	Methanation	$Nio-Al_2O_3$	Pyrophoric
9.	Ammonia synthesis	$Fe_3O_4-K_2OAl_2O_3-CaO$	Pyrophoric

Extraction of metals from spent catalysts

Fertilizer industry, spent catalyst contain alumina and metal such as Ni, Cu, Zn, Mo, Cu Fe and Co in appreciable concentrations. These metals are highly valuable and are used extensively in the steel industry and in the manufacture of special alloys. Spent catalysts could be used as a cheap source for the these valuable metals. This will result in recycling and reutilization of the waste catalysts and reduce their environmental and economic benefits, increasing attention has been paid to develop processes for recovering metals and other valuable materials from spent catalysts of fertilizers industry.

Several method such as chlorination, acid leaching, alkali leaching, roasting with soda salts etc. have been studied and reported for the recovery of metals (Co, Mo, Ni, Cu, Zn Fe) from the spent catalysts. Once in the solution, the metals can be isolated in a pure form using established method based on selective precipitation and solvent extraction. In case of solvent extraction, a high selectivity of extraction can be achieved by merely adjusting the pH of the solution containing an extracting agent (Inoue et al, 1993).

Metal reclaimers use one of two method hydrometallurgy and pyrometallurgy. Hydrometallurgy dissolves the metal by leaching the catalsyts with an acid or base the metals are then recovered as marketable metal compound or metals. Pyrometallury uses a heat treatment such as roasting or smelting to separate the metals. It melts the spent catalysts at high temperatures, often with the aid of a flux to lower the melting temperature and viscosity of the slag. The metals sink to the bottom of the melt and are recovered and sold. The catalysts base/ substrate floats on the surface as a slag that can be recovered and sold as a commercial commodity. The recovered metals could be used in steel manufacture and the alumina could be used for manufacture of refractories, ceramics and abrasives.

Production of useful materials from spent catalyts

Utilization of spent catalysts as raw materials in the production of valuable products is an attractive option for their recycling from environmental and economic point of view. The use of spent fluid catalytic craking catalyts in cement and concrete production has been reported in many studies, but the use of spent catalysts in cement production appears to be restricted because of its hazardous nature. However, many other useful materials such as fused alumina, synthetic aggregates, anorthite glas ceramics, refractory cement and refractory brick have been prepard from spent catalysts.

CONCLUSION

The above detail revealed that the spent catalysts generated from fertilizer industry can serve as a secondary source of recovery of metal. Recovery of valuable elements from spent catalysts become an unavoidable task not only for lowering the catalysts cost but also for reducing the catalysts waste to prevent the environmental pollution.

REFERENCES

1. Fertilizers Association of India 'Manual for pollution control and fertilizer industry part II' New Delhi, FAI (1987).
2. HPC, " A Report of High Powered Committee on Management of Hazardous Wastes", volume I (P351), Volume II (P569) and Volume III (P245) (2001).
3. CPCB, Criteria for hazardous waste landfils, Hazardous waste Management, Series: Hazwams /17/2000-01,P35 (2001).
4. S.Prakash Babu, A Narayanam, FAI Seminar, November 28-30 (2006.)
5. K.AI-Dalama, A.Stanistaus, Comaprison between deactivation patterns of catalysts in fixed bed and ebullating bed residue hydroprocessing units, *Chemical Engineering Journal* **120**: 33-42 (2006).
6. A.Marafi, A.Hauser, A.Stanislaus, Deactivation patterns of Mo/Al_2O_3, Ni-$MoAl_2O_3$ and Ni-MoP/Al_2O_3 catalysts in atmospheric residue hydro desulphurization, *Catalysts Today* **125**: 192-202 (2007) .
7. D.D. Sun, J.H. Tay, H.K. Cheong, D.L.K.Leung, G.Quian, Recovery of heavy metals and stabilization of spent hydrotreating catalyst using a glass-ceramic matrix, *Journal of Haardous Materials*, B**87**: 213-223. (2001).
8. B.B. Kar, B.V.R. Murthy, V.N. Mishra, Extraction of molybdenum from spent catalyst by salt roasting, *International Journal of Mineral Processing* **76**: 143-147 (2005).
9. S.A. Wasay, S.Barrington, S.Tokunaga, Organic acids for the in situ remediation of soils polluted by heavy metals: soil flushing columns, *Water Air and Soil Pollution* **127**:

301-314 (2001).

10. T.T. Lim, J.H. Tay, J.Y. Wang, Chealting agent enhanced heavy metal extraction from a contaminated acidic soil, *Journal of Environmental Engineering* **130**: 59-66 (2004).

11. M.Marafi, A.Stanislaus, Options and processes for spent catalyst handling and utilization, *Journal of Hazardous Materials* B**101**: 123-132 (2003).