Journal of Hazardous Materials 344 (2018) 169–178

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Research Paper

Process integration for material synthesis from a deactivated catalyst: Studies on the interaction of metal ions between two immiscible phases

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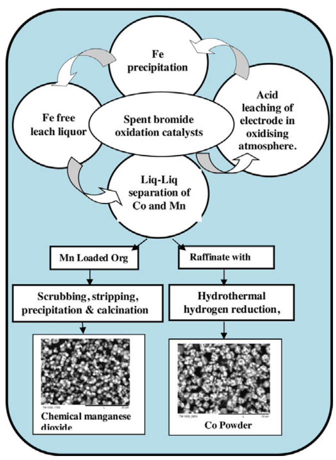
HIGHLIGHTS

- Spent Co-Mn-bromide catalyst was leached in acidic & oxidising condition to bring Co & Mn into the solution.
- Metals were extracted by solvent. Metal loaded organic was scrubbed for Co removal and Mn was stripped by dilute H_2SO_4.
- Stripped Mn solution was subjected to precipitation and calcined to give high pure CMD.
- Cobalt in raffinate was precipitated as hydroxide & hydrothermally reduced to produce cobalt powder.
- The leachate disposal after extraction and separation of metals was eco-friendly.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 May 2017
Received in revised form
23 September 2017
Accepted 25 September 2017
Available online 7 October 2017

Keywords:
Co–Mn bromide spent catalyst
Solvent extraction
Cobalt powder
Chemical manganese dioxide
Hydrothermal hydrogen reduction

ABSTRACT

Present investigation deals with the treatment of deactivated Co-Mn bromide catalyst for the recovery of Co and Mn as Co metal powder and chemical manganese dioxide by an integrated process comprising of a selective metal ion transfer from an aqueous solution containing a mixture of metal ions with a saponified solution of di-2ethyl-hexyl phosphoric acid, followed by selective scrubbing and metal stripping. The pure metal solutions so obtained were subjected to precipitation and hydrothermal treatment to obtain a desired material. The deactivated catalyst was leached by H_2SO_4 in presence of H_2O_2 followed by removing Fe, Si etc. The purified leach liquor of composition: 6.9 g/L Co, 9.4 g/L Mn was used for detail study to optimize the best conditions for the separation of Co from Mn. Experimental observations show that the extraction of both increased with increasing equilibrium pH and the concentration of the organic, with a separation factor of about 10, at equilibrium pH of 3. A quantitative extraction of

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https://doi.org/10.1016/j.jhazmat.2017.09.042

Mn was possible with 20% D2EHPA in three stage counter-current extraction. After Co scrubbing, Mn was stripped with dilute H_2SO_4 and high pure spherical shaped CMD was produced. Co in the raffinate was recovered as powder by hydrothermal H_2- reduction.

1. Introduction

With the increase in world's cobalt usage, and non availability of cobalt rich primary resources, cobalt is produced mostly as a by-product of other major metal extraction processes – such as recovery of manganese, copper and nickel – and in the recent decades various industrial scraps and metal-bearing wastes such as steel scrap, spent electrode, waste electrolyte, spent catalyst etc can be banked upon for the recovery of these valuable metal.

Similarly manganese separation is particularly important to recover it from secondary manganese containing materials including Mn-bearing steel scrap, spent electrode, waste electrolyte, spent catalyst etc. Co(II) and Mn(II) have many applications in various fields, for example steel production, aerobic organic synthesis [1] non-ferrous alloys, organic reactions [2], fertilizers, Co-Mn oxides for Li cells etc. The focus of the study in this work is the recovery of Co and Mn from spent catalyst, hence a brief brush-up on the catalyst is justified here.

1.1. A brief brush up on catalyst

Catalyst is a substance which only facilitates the chemical reaction without being consumed during its participation. Broadly these are of two types: homogeneous and Heterogeneous mainly distinguished by the different phases present during reaction and the third type is enzyme based catalyst. Homogeneous catalyst is present in the same phase as reactants and products, usually liquid, and heterogeneous catalyst is present in a different phase, usually solid. A pictorial representation for the classification of different types of catalysts is shown in Fig. 1. Recently Molnar and Papp [3] have reviewed the recent progress and current status on catalyst recycling. Another review on the currently available transition metal oxides, and their applications as a bi-functional catalyst for their utilization in fuel cells and rechargeable metal-air batteries in alkaline media has been compiled by Osgood et al. [4]. Imran et al. [5] have used Mn-Co-Zn based mixed-oxide spinels as novel catalysts for the chemical recycling of poly(ethylene terephthalate) via glycolysis.

The major chemical and physical properties differentiating heterogeneous and homogeneous catalysts are tabulated below(Table 1)

Table 1
Properties of homogeneous and heterogeneous catalysts.

Heterogeneous catalysts	Homogeneous catalysts
Phase of catalyst and reactant are different such as gas/solid; liquid/solid or liquid/liquid systems.	Same phase as reaction medium
Easily separated from the reaction mixture	Separation is very difficult and lengthy process
They can be used in a wide range of operating conditions with respect to range of temperatures/pressures and is thermally stable	Reaction conditions are milder ie from a low temperature of −78 °C to upto ~200 °C, and high pressure but thermal stability is very low
Active sites are not well defined and have limited accessibility	Molecular active sites are well defined, uniform, tuneable as per need and highly available
Reaction mechanism and kinetics is complex. Catalytic activity is difficult to establish and understand.	Reaction kinetics is fast. Catalytic activity and mechanism could be establish and understand.
Eco friendly and due to ease in operation they attract high industrial relevance and about 85–90% of all catalytic processes are heterogeneously catalyzed.	Damages the environment and its major use is in pharma, fines and specialty chemical manufacturing. Consumption is approx 15%
Sensitive to poisoning but can be recycled several times before its deactivation and can be readily regenerated/recycled.	Robust to poisons but sensitive to water and oxygen Service life is very short and Recycling is very difficult

Due to many favorable features of heterogeneous catalysts as mentioned above, different types of catalysts based on the process where it will be used, are made with different metal composition at different base material. Many industrial synthesis and processes require the use of catalysis. Huge quantities of catalysts are used in the fertiliser industry [6] (i.e., ammonia plants), petroleum refineries, the chemical sectors, various organic conversion processes, and automotive catalytic converters for pollution control [7]. Li et al. [8] have worked on the enhancement on the waste management of spent hydro-treating catalysts. There is an enormous importance of catalysis in chemical processes. The development of chemical products in advanced and industrialized society is technically, economically and ecologically possible by means of specific catalyst. 95% of all the products (by volume) are synthesized by means of catalysis, while 20% of the world economy depends directly or indirectly on catalysis. An estimated 70% of all the chemical processes are based on catalytic technologies, encompassing four major market sectors: fuel refining, polymerization, chemical production and environmental remediation such as Ni/Al_2O_3 catalyst used in steam reforming of methane, Fe/Cr oxide used in CO conversion, $MoO_3/CoO/Al_2O_3$ used in refinery processing, nickel catalysts are commonly used for various industrial processes such as hydrogenation reactions, hydro treating, steam reforming, and methanation. An extensive review on the application of heterogeneous catalysts for the oxidation reaction has been compiled by Ali et al. [9]. The most active catalysts for total oxidation of model aromatic (toluene) and oxidic (ethanol) organic compounds contain Ni–Mg–Mn, Ni–Cu–Mg–Mn and Co–Mn–Al. A review on the management of spent hydroprocessing catalyst is compiled by M Marafi and A Stanislaus [10]. Cobalt-manganese bromide catalysts are widely used in homogeneous oxidation processes, particularly for the oxidation of o-xylene to terephthalic acid. Huge amount of cobalt is consumed to produce this catalyst which is used every year in the production of terephthalic acid and its derivatives, which in turn results in the generation of large amounts of solid waste in the form of spent catalysts. Hence due to the outstanding advantages of catalysts in deoxidizing process, sulfur-fixing, alloying and several other industrial applications, there is a high amount of usage and deactivation of these catalysts, and since waste is an unavoidable integral part of any industrial process, posing pollution threats on the environment, stringent environmental laws/legislations are becoming a strong driving force towards the concept of industrial ecology all over the world which leads to significant thrust on the reuse/recycle and recovery of values from the waste. This concept suggests that any industrial systems should attempt to use