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Recovery of Mo and Ni from spent acrylonitrile catalysts using an oxidation leaching–chemical precipitation technique

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ABSTRACT

An oxalic acid ($H_2C_2O_4$) and hydrogen peroxide (H_2O_2) leaching–chemical precipitation process was developed to recover valuable metals from the spent acrylonitrile catalysts that primarily contain Mo, Ni, Fe and Bi. $H_2C_2O_4$ and H_2O_2 leaching studies indicated good leaching efficiencies for Mo and very low efficiencies for Ni because of the formation of soluble molybdenum oxalate complexes and a nickel oxalate (NiC_2O_4) precipitate, which was separated by filtration. Under the optimal leaching conditions ($H_2C_2O_4$ concentration of 1.25 mol/L, H_2O_2 concentration of 0.20 mol/L, leaching temperature of 50 °C, liquid-to-solid (L/S) ratio of 20 mL/g and leaching time of 2.5 h), 99.7% of Mo was dissolved into the liquid phase, and 98.4% of Ni remained in the residues. For purification, the molybdenum oxalate complexes in the leaching liquor were broken down by adding the emulsion of $Ca(OH)_2$ to form calcium molybdate ($CaMoO_4$) and calcium oxalate (CaC_2O_4) precipitates; molybdenum trioxide (MoO_3) was then recycled, followed by processes of acid dissolution, ammonium molybdate deposition, and calcining. The NiC_2O_4 in the leaching residues was dissolved and converted into soluble nickel-oxalate-ammonium complexes by adding ammonium hydroxide (NH_4OH), and pure NiC_2O_4 powders were obtained from the filtered liquor through an ammonia stilling process after filtration. In this case, 95% of the Mo and 97% of the Ni in the spent catalyst were recovered as MoO_3 and NiC_2O_4 with purities of 97.88% and 99.91%, respectively. Based on the results of the present study, a tentative process flow sheet is proposed.

1. Introduction

Mo and Ni are strategic metals that are widely used as catalysts in petroleum refining and in the petrochemical and chemical industries (Mishra et al., 2010). Acrylonitrile catalysts are multi-metal molybdates that consist of Mo with Bi, Ni, Fe, Co, and additives (e.g., Cr, Mg, Rb, K, Cs, P, B, Ce, Sb, and Mn) as promoters dispersed in porous SiO_2, which serves as a support material (Cespi et al., 2014). These catalysts play a critical role in propylene ammonia oxidation processes, which are involved in almost all of the currently used acrylonitrile production processes (Cespi et al., 2014; Schuh et al., 2014). In every catalytic operation, the activity of the catalysts gradually decreases, and the catalysts become inactive at a certain point because of the loss of active components or the accumulation of organics, Hg, Pb and As on their surfaces (Szymczycha-Madeja, 2011). A large quantity of spent acrylonitrile catalysts must be replaced by fresh catalysts every year. Spent acrylonitrile catalysts are considered hazardous materials because they contain toxic metals that can leach out during storage and in landfills (Singh, 2009). However, spent acrylonitrile catalysts can also be considered secondary resources because they contain valuable metals (50% w/w) (Cespi et al., 2014).

Numerous processes have been developed for protecting the environment and for recovering valuable metals from spent Mo-Ni catalysts (Huang et al., 2014; Kim et al., 2009; Mishra et al., 2010; Pradhan et al., 2013; Safarzadeh et al., 2012; Wang and Wang, 2010). Hydrometallurgical processes have attracted particular interest because they are more environmentally friendly than thermometallurgical processes as a result of their lower energy requirements, lower gas emissions and smaller amounts of waste generated and because their metals can be completely recovered (Kinoshita et al., 2003; Park et al., 2012). In traditional hydrometallurgical methods, the spent catalysts are initially calcined to convert the metal sulfides to metal oxides or sulfates and subsequently leached using a strong base or strong acid (Park et al., 2007; Park et al., 2012). However, these methods are still highly dependent on the leaching conditions, which typically involve a strict pretreatment procedure, high concentrations of leaching agents, high temperatures and/or high pressures. Currently, the main technical routes investigated for the separation and purification of Mo and Ni from leaching liquor are the solvent extraction method (Banda et al.,

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2012; Park et al., 2012), the selective precipitation method (Huang and Zhao, 2014; Huang et al., 2014; Li et al., 2012), and the resin ion-exchange method (Lu et al., 2014; Wang et al., 2014).

Whereas inorganic acids, alkalis, salt reagents and their combinations have been widely investigated as leaching agents (Huang et al., 2014; Parhi et al., 2013; Park et al., 2012; Ramirez et al., 2013), only a few studies (Mulak et al., 2006; Szymczycha-Madeja, 2011) have investigated the effects of oxalic acid ($H_2C_2O_4$) combined with H_2O_2 on the leaching of Mo and Ni from spent catalysts. In Szymczycha-Madeja's work, the leaching kinetics of Mo, Ni, V and Al from a spent hydrodesulfurization catalyst in a solution containing $H_2C_2O_4$ and H_2O_2 was investigated, but according to the experimental results, the leaching efficiencies of the metals were not high.

In addition to its general acid properties, $H_2C_2O_4$ was chosen because it is a chelating agent that forms metal complexes with certain metals to increase their leaching efficiency (Szymczycha-Madeja, 2011). H_2O_2 was chosen because it is a strong oxidant that has been demonstrated to oxidize low-valence metal sulfides under acidic conditions (Aydogan et al., 2007) and because it provides high metal leaching efficiencies without calcining as a pretreatment. Furthermore, $H_2C_2O_4$ and H_2O_2 are environmentally friendly because $H_2C_2O_4$ easily undergoes biological degradation and because, apart from water, no other reaction products are obtained during the process of sulfide oxidation by H_2O_2.

The primary purpose of the present investigation was to develop a new process flow for recovering all of the valuable metals from spent acrylonitrile catalysts using a hydrometallurgical method that employs $H_2C_2O_4$ and H_2O_2 mixed solutions as leaching agents. Separation and purification processes using the chemical precipitation method were also investigated to recover Mo and Ni, respectively.

2. Experiments

2.1. Chemicals and apparatus

The spent acrylonitrile catalyst used in this work was obtained from a petrochemical corporation in northeastern China. Deionized water was used wherever necessary during the experimental processes, and all the chemical reagents used in this study were of analytical grade and were produced by the Shanghai Lingfeng Chemical Reagent Co., Ltd. X-ray diffraction (XRD) patterns were obtained using a D/max 2550V. Metals in the aqueous phase were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Agilent 725ES).

2.2. Characterization of raw material

The spent acrylonitrile catalyst sample was sieved through a 100 mesh screen after drying. The chemical composition of the spent catalyst sample, shown in Table 1, was determined by ICP-AES using the microwave-assisted aqua regia digestion method (Niemela et al., 2012). The XRD pattern of the spent acrylonitrile catalyst sample is shown in Fig. 1. The major peaks in the XRD pattern correspond to $NiMoO_4$, MoO_3, and MoS_2; however, no characteristic diffraction peaks of Bi were present, even though ICP-AES indicated that the sample contained 1.80% Bi.

Table 1
Composition of spent acrylonitrile catalyst (wt.%).

element	Mo	Ni	Fe	Bi	Mg	Zn	Cr	Pb	As
wt.%	22.3	7.20	2.86	1.80	0.87	0.0010	0.0016	0.010	0.11

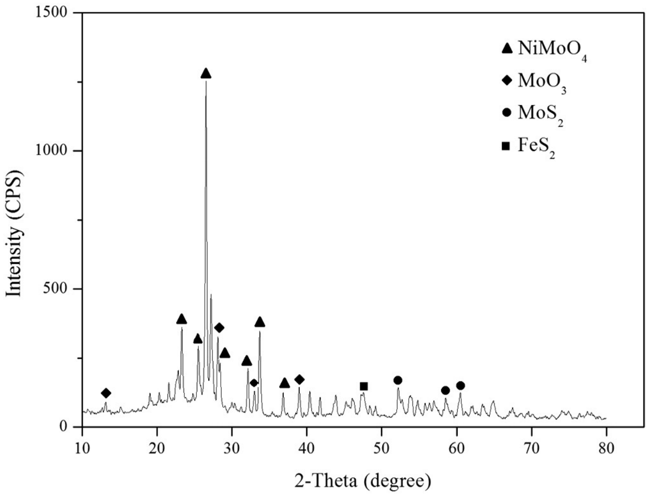

Fig. 1. XRD pattern of the spent acrylonitrile catalyst sample.

2.3. General experimental procedure

2.3.1. Leaching experiments

Leaching studies were conducted in stoppered glass reactors oscillated by a gas bath thermostatic oscillator to investigate the effects of the $H_2C_2O_4$ and H_2O_2 concentrations, liquid-to-solid (L/S) ratio, leaching temperature and leaching time on the leaching efficiencies of Mo and Ni. One milliliter of leaching liquor was collected for ICP-AES determination of the metal ion concentrations after the reactor was allowed to naturally cool to room temperature (25 °C) over a period of 2 h. Leaching experiments were conducted in triplicate, and the final result was the average of the three obtained values. Blank samples were analyzed throughout the entire procedure.

2.3.2. Purification experiments

For Mo purification, the emulsion of $Ca(OH)_2$ was added to the leaching liquor to break down molybdenum oxalate complexes and precipitate them as $CaMoO_4$ and CaC_2O_4. The resulting CaC_2O_4 and $CaMoO_4$ precipitates were treated with excess 50% (v/v) HNO_3 to decompose the $CaMoO_4$ into a soluble Mo solution, whereas CaC_2O_4 was insoluble and could be removed by filtration. The resulting filter liquor was neutralized with 50% (v/v) ammonia to precipitate and remove Ca^{2+} and other metal ions. The Mo-containing solution was acidified using

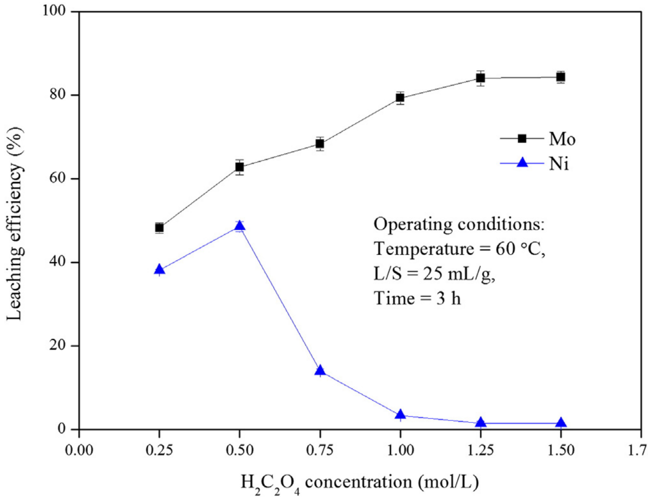

Fig. 2. Effect of $H_2C_2O_4$ concentration on Mo and Ni leaching efficiencies.